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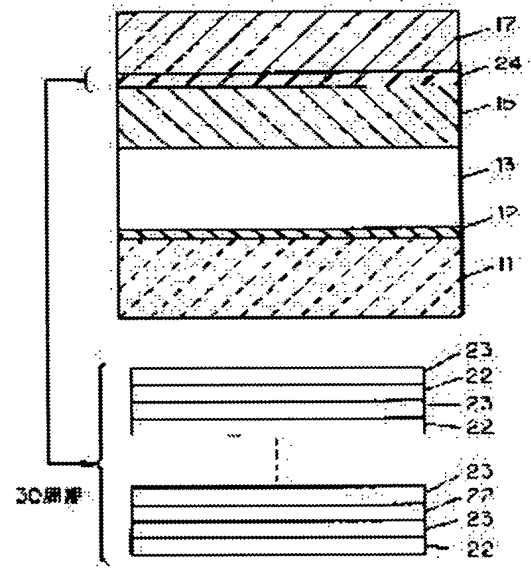
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(54) FORMATION OF SEMICONDUCTOR THIN FILM

(57)Abstract:

PURPOSE: To provide a formation method of an AlGaInN thin film of high quality which has little dislocation and point defects and is suitable for manufacture of a blue-color semiconductor laser element.

CONSTITUTION: A carbide layer continuously changing from Si to SiC is formed by setting the revolving speed of a heater on which a substrate is located to 300 rpm or higher, and feeding a methane gas onto an Si substrate 11 heated to 1200° C. The temperature is lowered to less than 600° C, and a GaN non-single crystal 12 20nm thick is formed. Then, a GaN layer 13 is formed with a substrate temperature not lower than 900° C, and an AlGaInN layer 15 for lattice matching with the GaN layer 13 is formed on the GaN layer with a substrate temperature set within a range of 300-900° C. To form the AlGaInN thin film, an alkylamine based material, a hydrazine based material, or a mixture of an alkylamine based material, a hydrazine based material and ammonia, is used as a nitrogen material. Thus, an AlGaInN thin film of high quality with little dislocation and point defects can be formed at low temperatures.



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CLAIMS

[Claim(s)]

[Claim 1] In the approach of supplying the raw material containing the raw material containing 3 group configuration element, and nitrogen, and forming an AlGaInN thin film through a buffer coat on the heated substrate front face The rotational speed of the heating object which has arranged said substrate is 300 or more revolutions per minute. It is the approach of forming a GaN layer at the substrate temperature of 900 degrees C or more, and forming an AlGaInN layer on said GaN layer at the substrate temperature set up within the limits of 300-900 degrees C. Formation of said AlGaInN layer is the formation approach of the AlGaInN thin film characterized by using the mixed raw material of an alkylamine system, a hydrazine system or an alkylamine system, a hydrazine system, and ammonia as a nitrogen raw material.

[Claim 2] The raw material containing the raw material containing 3 group configuration element and nitrogen is supplied on the heated substrate front face. In the approach of forming the AlGaInN multilayers which consist of an Alx1Gay1Inz1N layer / Alx2Gay2Inz2N layer / Alx3Gay3Inz3N layer (Eg2<Eg1 and Eg3:Eg are a band gap) through a buffer coat The rotational speed of the heating object which has arranged said substrate is 300 or more revolutions per minute. A GaN layer is formed at the substrate temperature of 900 degrees C or more. The Alx3Gay3Inz3N layer which carries out lattice matching to the Alx1Gay1Inz1N layer which carries out lattice matching to said GaN layer at the substrate temperature set up within the limits of 300-900 degrees C on said GaN layer, 2% or less of Alx2Gay2Inz2N layer which carries out grid mismatching, and said GaN layer It is the formation approach of the AlGaInN multilayers characterized by being the approach of forming and formation of said AlGaInN multilayers using the mixed raw material of an alkylamine system, a hydrazine system or an alkylamine system, a hydrazine system, and ammonia as a nitrogen raw material.

[Claim 3] The formation approach of the AlGaInN thin film which the rotational speed of the heating object which has arranged said substrate is 300 or more revolutions per minute, and is characterized by to arrange the strained layer superlattice structure which consists of an AlGaInN layer in said GaN layer and on a GaN layer in the approach of supplying the raw material containing the raw material containing 3 group configuration element, and nitrogen on the heated substrate front face, forming a GaN layer through a buffer coat, and forming an AlGaInN thin film on said GaN layer.

[Claim 4] An AlGaInN layer is the formation approach of the AlGaInN thin film given [the 1st and 3] in a claim characterized by forming by repeat supply of the raw material which supplies the raw material containing 3 group configuration element intermittently, and constitutes an InN layer and an AlGaN layer, and the formation approach of the AlGaInN multilayers the 2nd publication.

[Claim 5] The formation approach of the AlGaInN thin film characterized by making the carbonization layer which heated said substrate in the ambient atmosphere of the raw material containing hydrogen gas and carbon in the approach of supplying the raw material containing the raw material containing 3 group configuration element, and nitrogen, and forming an AlGaInN thin film through a buffer coat on the heated substrate front face, and was formed on said substrate front face into a buffer coat.

[Claim 6] In the approach of supplying the raw material containing the raw material containing 3 group configuration element, and nitrogen, and forming an AlGaInN thin film through a buffer coat on the heated substrate front face Subsequently with the carbonization layer which heated said substrate in the ambient atmosphere of the raw material containing carbon, and was formed on said substrate front face, an alkylamine system, The formation approach of the AlGaInN thin film characterized by making into a buffer coat at least the nitrated case formed on said carbonization layer front face in the ambient atmosphere

containing the mixed raw material of a hydrazine system or an alkylamine system, a hydrazine system, and ammonia.

[Claim 7] In the approach of supplying the raw material containing the raw material containing 3 group configuration element, and nitrogen, and forming an AlGaInN thin film through a buffer coat on the heated substrate front face An alkylamine system, a hydrazine system or an alkylamine system, a hydrazine system, the nitrated case formed on said substrate front face in the ambient atmosphere containing the mixed raw material of ammonia, the raw material which subsequently contains 3 group configuration element and an alkylamine system, The formation approach of the AlGaInN thin film characterized by making into a buffer coat the GaN non-single crystal layer formed on said nitrated case front face in the ambient atmosphere containing the mixed raw material of a hydrazine system or an alkylamine system, a hydrazine system, and ammonia.

[Claim 8] The manufacture approach of an AlGaInN thin film given in the 5-7th either of the claims characterized by making into 300 or more revolutions per minute rotational speed of the heating object which has arranged the substrate.

[Claim 9] The formation approach of an AlGaInN thin film given in the 1st, 3, 4, 5, 6, or the claim characterized by substrates being sapphire, SiC, ZnO and Si, GaAs, and GaP and InP 7.

[Claim 10] The formation approach of the AlGaInN multilayers according to claim 2 characterized by substrates being sapphire, SiC, ZnO and Si, GaAs, and GaP and InP.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates [the blue which can be used for the light source for information processors, such as green / blue light emitting diode and an optical disk, or] to the thin film formation approach of a nitride system ingredient about the manufacture approach of the semiconductor laser component of short wavelength further.

[0002]

[Description of the Prior Art] Since 670nm band AlGaInP system red semiconductor laser was commercialized in 1988, development of short wavelength semiconductor laser has been actively performed as the light sources for information processors, such as a laser beam printer and an optical disk. Although the core of development was 670-690nm at the beginning, a wavelength field is shifting to helium-Ne gas laser and 630nm band of this level with the demand of an improvement of the visibility of a bar code reader, the densification of an optical disk, etc. Furthermore, it will be anxious for the semiconductor laser implementation ranging from the blue and green to an ultraviolet area of short wavelength from red with increase of storage capacity in the future, and research of 2-6 group system semiconductor laser has been progressing quickly ignited by p mold conductivity-type control having been attained. On the other hand, although gallium nitride (GaN) was an ingredient promising as a light emitting device ranging from the blue to an ultraviolet region in the compound semiconductor of a direct transition mold with about 3.4eV extensive energy gap, since a GaN bulk substrate crystal could not produce easily but there was no substrate crystal good otherwise, the development as semiconductor laser was seldom progressing.

[0003] as the production approach of a GaN thin film — an alpha-aluminum 2O3 (sapphire) substrate top —

– MOVPE — generally the approach of carrying out vapor growth by law (metal–organic chemical vapor deposition) is used. It is going to decompose, and this tends to make trimethylgallium and ammonia react on the substrate heated at about 1050 degrees C, for example, a sapphire front face, and tends to grow a GaN thin film. It was proved recently using C (0001) side of sapphire that a comparatively good GaN thin film could be formed through GaN or an AlN non–single crystal layer. However, since the difference of the very big grid mismatching of 13.8% or a big coefficient of thermal expansion was between a sapphire C side and GaN, when a non–single crystal layer was minded, although relaxation of grid mismatching was started efficiently, two or more [108cm –] misfit rearrangements still existed, and it was not completed. [of quality thin film formation]

[0004] As compared with that everything but the good substrate crystal which carries out lattice matching of the trouble when carrying out crystal growth of the AlGaInN mixed–crystal thin film containing aluminum and In of 4 yuan as mentioned above not existing has the low decomposition effectiveness of the ammonia used as a nitrogen raw material, and the growth temperature of AlN and GaN, the decomposition temperature of InN is collected by that it is low temperature rather than them.

[0005] Since disassembly of ammonia took an elevated temperature, substrate temperature needed to be made into 900–1100 degrees C as mentioned above. For this reason, the hole of much nitrogen was generated in the film, and if the grown–up GaN layer remained as it was, it became the thin film in which n–type conduction nature is shown, and had the fault that the GaN thin film of high resistance was hard to be obtained. Therefore, compared with 1000 to 5000, and other ingredient systems, the so–called double figures of of the delivery late of three groups and five groups, and a 3 / 5 ratios needed to be enlarged from a single figure. Although it was desirable to grow up at low temperature as much as possible, since decomposition temperature was very high, even when growing up at low temperature, very a lot of ammonia is required for ammonia, and it had exceeded the range which can be supplied practical.

[0006] Moreover, when AlGaInN is grown up at about 1000 degrees C using ammonia, since decomposition effectiveness of ammonia is low, In tends to be desorbed from a substrate front face. There was a fault that control of a presentation was difficult, and brought about degradation of surface morphology, and the AlGaInN thin film of high quality could not be easily obtained by decomposition of InN since the amount of incorporation of In is remarkable and there are. [few]

[0007]

[Problem(s) to be Solved by the Invention] According to the above–mentioned conventional technique, since ammonia was used as a raw material of the nitrogen, it was not able to grow up to be the crystal growth of a nitride by whenever [low–temperature] comparatively. Therefore, at the time of MOVPE growth, the big heat convection occurred on the substrate, the uniform feeding to a substrate top was difficult, and control of the conduction type by the impurity dope, i.e., growth of the nitride of p mold conduction, was difficult. This invention makes possible crystal growth which was excellent in the controllability with low temperature, and aims at offering the formation approach of the AlGaInN thin film in which it is possible to obtain a good AlGaInN thin film with few holes of nitrogen, and the conduction type control which can be easily made into an n–type conduction mold or p mold conductivity by the impurity dope is possible. It sets it as the main purposes to offer the formation approach of the AlGaInN thin film containing especially In.

[0008] Moreover, according to the conventional technique, since [that it is bad and] the difference of a coefficient of thermal expansion of the adjustment of the lattice constant of a nitride and silicon on sapphire was also large, a pit and a crack tended to go into the grown–up nitride, it was uniform, and growth of the good nitride of surface smoothness was difficult for it.

[0009] This invention can carry out thin film formation at low temperature conventionally, and aims at a rearrangement offering the formation approach of few good AlGaInN thin films of surface smoothness.

[0010] Furthermore, according to the conventional technique, sapphire was used as a substrate, but processing was difficult and production of a device was not easy. This invention is cheap, is uniform on the easy substrate of processing, and aims at offering the formation approach of the good AlGaInN thin film of surface smoothness.

[0011]

[Means for Solving the Problem] In order to attain the above–mentioned purpose, the formation approach of an AlGaInN thin film according to claim 1 In the approach of supplying the raw material containing the raw material containing 3 group configuration element, and nitrogen, and forming an AlGaInN thin film through a buffer coat on the heated substrate front face The rotational speed of the heating object which has arranged said substrate is 300 or more revolutions per minute. It is the approach of forming a GaN

layer at the substrate temperature of 900 degrees C or more, and forming an AlGaInN layer on said GaN layer at the substrate temperature set up within the limits of 300–900 degrees C. It is characterized by formation of said AlGaInN layer using the mixed raw material of an alkylamine system, a hydrazine system or an alkylamine system, a hydrazine system, and ammonia as a nitrogen raw material.

[0012] The production approach of AlGaInN multilayers according to claim 2 The raw material containing the raw material containing 3 group configuration element and nitrogen is supplied on the heated substrate front face. In the approach of forming the AlGaInN multilayers which consist of an Al_x1Gay1Inz1N layer / Al_x2Gay2Inz2N layer / Al_x3Gay3Inz3N layer (Eg2<Eg1 and Eg3:Eg are a band gap) through a buffer coat The rotational speed of the heating object which has arranged said substrate is 300 or more revolutions per minute. A GaN layer is formed at the substrate temperature of 900 degrees C or more. The Al_x3Gay3Inz3N layer which carries out lattice matching to the Al_x1Gay1Inz1N layer which carries out lattice matching to said GaN layer at the substrate temperature set up within the limits of 300–900 degrees C on said GaN layer, 2% or less of Al_x2Gay2Inz2N layer which carries out grid mismatching, and said GaN layer It is the approach of forming and is characterized by formation of said AlGaInN multilayers using the mixed raw material of an alkylamine system, a hydrazine system or an alkylamine system, a hydrazine system, and ammonia as a nitrogen raw material.

[0013] The production approach of an AlGaInN thin film according to claim 4 and multilayers is characterized by forming an AlGaInN layer by repeat supply of the raw material which supplies the raw material containing 3 group configuration element intermittently, and constitutes an InN layer and an AlGaIn layer in the formation approach of an AlGaInN thin film given [the 1st and 3] in a claim, and the formation approach of the AlGaInN multilayers the 2nd publication.

[0014] The formation approach of an AlGaInN thin film according to claim 3 In the approach of supplying the raw material containing the raw material containing 3 group configuration element, and nitrogen on the heated substrate front face, forming a GaN layer through a buffer coat, and forming an AlGaInN thin film on said GaN layer The rotational speed of the heating object which has arranged said substrate is 300 or more revolutions per minute, and it is characterized by arranging the strained layer superlattice structure which consists of an AlGaInN layer in said GaN layer and on a GaN layer.

[0015] The formation approach of an AlGaInN thin film according to claim 5 is characterized by to make into a buffer coat the carbonization layer which heated said substrate in the ambient atmosphere of the raw material containing hydrogen gas and carbon, and was formed on said substrate front face in the approach of supplying the raw material containing the raw material containing 3 group configuration element, and nitrogen, and forming an AlGaInN thin film through a buffer coat on the heated substrate front face.

[0016] The formation approach of an AlGaInN thin film according to claim 6 In the approach of supplying the raw material containing the raw material containing 3 group configuration element, and nitrogen, and forming an AlGaInN thin film through a buffer coat on the heated substrate front face Subsequently with the carbonization layer which heated said substrate in the ambient atmosphere of the raw material containing carbon, and was formed on said substrate front face, an alkylamine system, It is characterized by making into a buffer coat at least the nitrated case formed on said carbonization layer front face in the ambient atmosphere containing the mixed raw material of a hydrazine system or an alkylamine system, a hydrazine system, and ammonia.

[0017] The formation approach of an AlGaInN thin film according to claim 7 In the approach of supplying the raw material containing the raw material containing 3 group configuration element, and nitrogen, and forming an AlGaInN thin film through a buffer coat on the heated substrate front face An alkylamine system, a hydrazine system or an alkylamine system, a hydrazine system, the nitrated case formed on said substrate front face in the ambient atmosphere containing the mixed raw material of ammonia, the raw material which subsequently contains 3 group configuration element and an alkylamine system, It is characterized by making into a buffer coat the GaN non-single crystal layer formed on said nitrated case front face in the ambient atmosphere containing the mixed raw material of a hydrazine system or an alkylamine system, a hydrazine system, and ammonia.

[0018] As for the rotational speed of the heating object which has arranged the substrate, in the above claim, it is desirable to consider as 300 or more revolutions per minute. Moreover, as for a substrate, it is desirable that they are sapphire, SiC, ZnO and Si, GaAs, and GaP and InP.

[0019]

[Function] One of the troubles in the crystal growth of an AlGaInN thin film is that the decomposition temperature of InN is low temperature from them as compared with the growth temperature of AlN and

GaN. That is, when an AlGaInN thin film is grown up at the growth temperature of an AlGaIn thin film using ammonia, since decomposition effectiveness of ammonia is low, In tends to be desorbed from a substrate front face. By decomposition of InN, since the amount of incorporation of In is remarkable and there are, control of a presentation is difficult and brings about degradation of surface morphology. [few]

[0020] Since high-speed rotation of the substrate was carried out using the nitrogen raw material which contains an alkylamine system with low decomposition temperature, and a hydrazine system at least according to the production approach of the AlGaInN thin film of claim 1, and the production approach of the AlGaInN multilayers of claim 2, it can grow up at low temperature comparatively, and control of the gas convection current by the high thing and the control of dissociation of In of growth temperature are attained. Therefore, formation of a quality AlGaInN thin film or AlGaInN multilayers is attained from the former at low temperature.

[0021] supplying material gas on a substrate by turns like In, N/N/Ga, aluminum, and N/N at low temperature using the nitrogen raw material containing the mixed raw material of an alkylamine system, a hydrazine system or an alkylamine system, a hydrazine system, and ammonia according to the production approach of the AlGaInN thin film of claim 3 — a nitrogen hole — few — picking ** rare ** of In — since it becomes stable, formation of a quality AlGaInN thin film or AlGaInN multilayers is attained from the former at low temperature.

[0022] One of the troubles in the crystal growth of an AlGaInN thin film is that there is no lattice matching substrate. Although the nitride thin film was conventionally formed through the non-single crystal layer of AlN or GaN on silicon on sapphire, silicon on sapphire is difficult to process it, and it is unsuitable as a substrate for semiconductor devices. And between AlN or a GaN non-single crystal layer, since still big grid mismatching and heat distortion exist, propagation of the rearrangement generated in the interface with a substrate cannot be controlled enough.

[0023] Since according to the production approach of the AlGaInN thin film of claim 4 the AlGaInN superlattice containing distortion is arranged before carrying out AlGaInN thin film formation, since the movement component to field inboard becomes large, the rearrangement generated from the substrate interface can control the propagation to an up layer efficiently, and can form a quality AlGaInN thin film.

[0024] According to the production approach of the AlGaInN thin film of claims 5 and 6, carbon is spread in a substrate during heat treatment performed before forming an AlGaInN thin film, for example on a silicon substrate, and when silicon dissociates from the inside of a substrate, the carbonization layer which carries out continuous presentation change from silicon to SiC can be formed. Since generating of a rearrangement is controlled since the lattice constant of SiC is as near as the lattice constant of a nitride, and there is effectiveness also in relaxation of heat distortion, propagation of the rearrangement to an AlGaInN thin film can be reduced sharply.

[0025] According to the production approach of the AlGaInN thin film of claim 7, nitrogen is spread in a substrate during heat treatment performed before forming an AlGaInN thin film, for example on a GaP substrate, and when P dissociates from the inside of a substrate, the nitrated case which carries out continuous presentation change from GaP to GaN can be formed. Furthermore, since the non-single crystal layer of GaN is formed, the nucleus to which homogeneity and particle size were equal can be formed. For this reason, since generating of a rearrangement is controlled and there is effectiveness also in relaxation of heat distortion, propagation of the rearrangement to an AlGaInN thin film can be reduced sharply.

[0026] Thus, the formation of an AlGaInN thin film quality also on the easy substrate of the other processing, for example, a silicon substrate, and a GaP substrate including sapphire is possible.

[0027] Therefore, this invention is very useful to the blue semiconductor laser component manufacture which can be used for high blue light emitting diode, the light source for information processors, etc. of luminous efficiency.

[0028]

[Example] Hereafter, an example explains this invention. In addition, about the same part, the same sign is described below.

[0029] The MOVPE equipment roughly shown in drawing 1 was used for manufacture of an AlGaInN thin film. Here, the gas installation tubing 2 made from a quartz is attached in the interior of the coil 1 made from a quartz. From gas installation tubing made from a quartz, the raw material containing the raw material containing 3 group configuration element and nitrogen can be supplied now to coincidence. The coil 3 for high-frequency heating is installed in the periphery of the coil 1 made from a quartz, and the susceptor 4 made from graphite by which the SiC coat was carried out is installed in the interior. The susceptor 4 made from graphite is supported by the motor by the susceptor bearing bar 5 pivotable to 1000 revolution-per-

minute extent. It has the composition that the substrate 7 carried on the tray 6 made from a quartz can be installed in susceptor 4 made from graphite top face. Moreover, the exhaust port 8 connected to the vacuum pump is established in the pars basilaris ossis occipitalis of the coil 1 made from a quartz, and it has come to be able to perform the pressure regulation in the coil 1 made from a quartz, and exhaust air of gas.

[0030] (Example 1) Cross-section structural drawing of the AlGaInN thin film produced by the formation approach of the AlGaInN thin film of the first example of this invention to drawing 2 is shown. About the formation approach of the AlGaInN thin film using the MOVPE equipment of drawing 1, order is explained later on.

[0031] (111) After carrying out organic washing of the field silicon substrate 11, it has arranged as a crystal growth substrate on the tray 6 made from a quartz, and introduced in the coil 1 made from a quartz. After introducing hydrogen gas in the coil 1 made from a quartz, coil 1 made from a quartz internal pressure was set as 1/10 atmospheric pressure, and the susceptor 4 made from graphite was rotated by 800 revolutions per minute. The temperature up of the susceptor 4 made from graphite was carried out to 1200 degrees C in hydrogen gas, and silicon substrate 11 front face was defecated. After lowering substrate temperature to 600 degrees C, the hydrazine was introduced as a V group raw material on the 11th page of a silicon substrate from the gas installation tubing 2 made from a quartz, and trimethylgallium was introduced as 3 group raw materials after 1 minute. Installation of trimethylgallium was suspended after depositing the non-single crystal GaN layer 12 of 20nm of thickness. This was used as a buffer coat. Subsequently, the temperature up of the substrate temperature was carried out to 1000 degrees C, in addition to the hydrazine, ammonia was introduced as a V group raw material, and trimethylgallium was introduced as 3 group raw materials after 1 minute. Installation of trimethylgallium was suspended after growing up the GaN layer 13 of 3 micrometers of thickness. When 3 micrometers grew, GaN layer 13 front face became flat, and propagation of the defect generated from the substrate interface was reduced remarkably. Subsequently, substrate temperature was lowered at 800 degrees C, trimethylgallium, trimethylaluminum, and trimethylindium were introduced into coincidence, and aluminum_{0.45}Ga_{0.5}In_{0.05}N layer 14 of 0.5 micrometers of thickness was grown up. After suspending installation of trimethylgallium, trimethylaluminum, and trimethylindium, installation of a hydrazine and ammonia was suspended in the place which lowered substrate temperature and became the temperature of 300 degrees C or less. After dropping the temperature of a substrate to a room temperature, the substrate was taken out from the inside of the coil 1 made from a quartz.

[0032] The obtained crystal front face was uneven, when rotating the susceptor 4 made from graphite by 10 revolutions per minute, to In presentation of a mixed-crystal layer having been 0.02, in the case of this example, there was little adhesion of a resultant in the gas installation tubing 2 made from a quartz, a lot of resultants adhered to the gas installation tubing 2 made from a quartz, and, as for carrier concentration, according to the hall effect, 10^{15}cm^{-3} and the 4 yuan mixed crystal with very few defects of 4 yuan were obtained in the mirror plane. Moreover, it checked that In presentation was set to 0.05, In was incorporated by high-speed rotation of 800 revolutions per minute, and a rate increased. Though it was 800 degrees C and low temperature, the mixed crystal of 4 yuan more nearly quality than the GaN layer which grew at 1000 degrees C was obtained. it is the depressor effect of reduction of the nitrogen hole by these results having introduced a hydrazine and ammonia into coincidence, and dissociation of In, and convection-current control of the gas stream by high-speed rotation and a raw material are efficient — it is thought that it depends for incorporating.

[0033] (Example 2) It is cross-section structural drawing of the AlGaInN multilayers produced by the formation approach of the AlGaInN multilayers of the second example of this invention to drawing 3. About the formation approach of AlGaInN multilayers using the MOVPE equipment of drawing 1, order is explained later on.

[0034] (111) After carrying out organic washing of the field silicon substrate 11, it has arranged as a crystal growth substrate on the tray 6 made from a quartz, and introduced in the coil 1 made from a quartz. After introducing hydrogen gas in the coil 1 made from a quartz, coil 1 made from a quartz internal pressure was set as 1/10 atmospheric pressure, and the susceptor 4 made from graphite was rotated by 800 revolutions per minute. The temperature up of the susceptor 4 made from graphite was carried out to 1200 degrees C in hydrogen gas, and silicon substrate 11 front face was defecated. After lowering substrate temperature to 600 degrees C, the hydrazine was introduced as a V group raw material on the 11th page of a silicon substrate from the gas installation tubing 2 made from a quartz, and trimethylgallium was introduced as 3 group raw materials after 1 minute.

[0035] Installation of trimethylgallium was suspended after depositing the non-single crystal GaN layer 12 of 20nm of thickness. This was used as a buffer coat. Subsequently, the temperature up of the substrate temperature was carried out to 1000 degrees C, in addition to the hydrazine, ammonia was introduced as a V group raw material, and trimethylgallium was introduced as 3 group raw materials after 1 minute. Installation of trimethylgallium was suspended after growing up the GaN layer 13 of 3 micrometers of thickness.

[0036] When 3 micrometers grew, GaN layer 13 front face became flat, and propagation of the defect generated from the substrate interface was reduced remarkably. Subsequently, substrate temperature was lowered at 800 degrees C, trimethylgallium, trimethylaluminum, and trimethylindium were introduced into coincidence, and aluminum_{0.45}Ga_{0.5}In_{0.05}N layer 15 of 1.0 micrometers of thickness which carried out lattice matching to the GaN layer 13 was grown up. After suspending installation of trimethylgallium, trimethylaluminum, and trimethylindium, substrate temperature was lowered to 700 degrees C, trimethylgallium and trimethylindium were introduced into coincidence, and Ga_{0.8}In_{0.2}N layer 16 of 0.01 micrometers of thickness with a stacking fault was grown up. Subsequently, after suspending installation of trimethylgallium and trimethylindium, the temperature up of the substrate temperature was carried out to 800 degrees C, trimethylgallium, trimethylaluminum, and trimethylindium were introduced into coincidence, and aluminum_{0.45}Ga_{0.5}In_{0.05}N layer 17 of thickness 1.0um which carried out lattice matching to the GaN layer 13 was grown up again. After suspending installation of trimethylgallium, trimethylaluminum, and trimethylindium, installation of a hydrazine and ammonia was suspended in the place which lowered substrate temperature and became the temperature of 300 degrees C or less. After dropping the temperature of a substrate to a room temperature, the substrate was taken out from the inside of the coil 1 made from a quartz.

[0037] The front face of the obtained AlGaInN multilayers is a mirror plane, and checked strong luminescence from Ga_{0.8}In_{0.2}N layer 16 as a result of photoluminescence measurement.

[0038] When rotating the susceptor 4 made from graphite by 10 revolutions per minute, a lot of resultants adhere to the gas installation tubing 2 made from a quartz, the obtained crystal front face was uneven, In presentation was set to 0.2, In was incorporated by rotation of 800 revolutions per minute, and increase of a rate was checked [in the case of this example, there was little adhesion of a resultant in the gas installation tubing 2 made from a quartz to In presentation of a GaInN layer having been 0.12,]. Though it was 800 degrees C and low temperature, the multilayers containing In more nearly quality than GaN which grew at 1000 degrees C were obtained. it is the depressor effect of reduction of the nitrogen hole by these results having introduced a hydrazine and ammonia into coincidence, and dissociation of In, and convection-current control of the gas stream by high-speed rotation and a raw material are efficient — it is thought that it depends for incorporating.

[0039] Moreover, formation of multilayers was possible, maintaining crystallinity comparable as lattice matching mixed crystal, even if it introduced GaInN with a stacking fault.

[0040] (Example 3) Cross-section structural drawing of the AlGaInN thin film produced by the formation approach of the AlGaInN thin film of the third example of this invention to drawing 4 is shown. About the manufacture approach of the AlGaInN thin film using the MOVPE equipment of drawing 1, order is explained later on.

[0041] (111) After carrying out organic washing of the field silicon substrate 11, it has arranged as a crystal growth substrate on the tray 6 made from a quartz, and introduced in the coil 1 made from a quartz. After introducing hydrogen gas in the coil 1 made from a quartz, coil 1 made from a quartz internal pressure was set as 1/10 atmospheric pressure, and the susceptor 4 made from graphite was rotated by 800 revolutions per minute. The temperature up of the susceptor 4 made from graphite was carried out to 1200 degrees C in hydrogen gas, and silicon substrate 11 front face was defecated. After lowering substrate temperature to 600 degrees C, the hydrazine was introduced as a V group raw material on the 11th page of a silicon substrate from the gas installation tubing 2 made from a quartz, and trimethylgallium was introduced as 3 group raw materials after 1 minute. Installation of trimethylgallium was suspended after depositing the non-single crystal GaN layer 12 of 20nm of thickness. This was used as a buffer coat.

[0042] Subsequently, the temperature up of the substrate temperature was carried out to 1000 degrees C, in addition to the hydrazine, ammonia was introduced as a V group raw material, and trimethylgallium was introduced as 3 group raw materials after 1 minute. Installation of trimethylgallium was suspended after growing up the GaN layer 13 of 3 micrometers of thickness. When 3 micrometers grew, GaN layer 13 front face became flat, and propagation of the defect generated from the substrate interface was reduced remarkably. Subsequently, substrate temperature was lowered at 800 degrees C, trimethylgallium and

trimethylaluminum were introduced into coincidence, and aluminum_{0.3}Ga_{0.7}N layer 18 of 2nm of thickness was grown up. After suspending installation of trimethylgallium and trimethylaluminum, trimethylgallium and trimethylindium were introduced into coincidence and Ga_{0.8}In_{0.2}N layer 19 of 2nm of thickness was grown up. After growing up the aluminum_{0.3}Ga_{0.7}N/Ga_{0.8}In_{0.2}N strained layer superlattice 20 of 40 periods continuously, trimethylgallium was introduced again, the GaN layer 21 of 2 micrometers of thickness was grown up, and installation of trimethylgallium was suspended. Subsequently, trimethylgallium, trimethylaluminum, and trimethylindium were introduced into coincidence and aluminum_{0.45}Ga_{0.5}In_{0.05}N layer 14 of 0.5 micrometers of thickness was grown up. After suspending installation of trimethylgallium, trimethylaluminum, and trimethylindium, installation of a hydrazine and ammonia was suspended in the place which lowered substrate temperature and became the temperature of 300 degrees C or less. After dropping the temperature of a substrate to a room temperature, the substrate was taken out from the inside of the coil 1 made from a quartz.

[0043] By introducing the aluminum_{0.3}Ga_{0.7}N/Ga_{0.8}In_{0.2}N strained layer superlattice 20, propagation of the defect generated from the substrate interface was controlled remarkably, and the defect of about double [more] figures was reduced compared with the case of an example 1. According to [in the obtained crystal front face] the hall effect in a mirror plane, carrier concentration is three or less [10^{15}cm^{-3}], and the GaN layer growth temperature grew up to be at 1000 degrees C though it was 800 degrees C and low temperature, and 4 yuan mixed crystal still more nearly quality than the case of an example 1 were obtained.

[0044] (Example 4) It is cross-section structural drawing of the AlGaInN multilayers produced by the formation approach of the AlGaInN multilayers of the fourth example of this invention to drawing 5. About the formation approach of AlGaInN multilayers using the MOVPE equipment of drawing 1, order is explained later on.

[0045] (111) After carrying out organic washing of the field silicon substrate 11, it has arranged as a crystal growth substrate on the tray 6 made from a quartz, and introduced in the coil 1 made from a quartz. After introducing hydrogen gas in the coil 1 made from a quartz, coil 1 made from a quartz internal pressure was set as 1/10 atmospheric pressure, and the susceptor 4 made from graphite was rotated by 800 revolutions per minute. The temperature up of the susceptor 4 made from graphite was carried out to 1200 degrees C in hydrogen gas, and silicon substrate 11 front face was defecated. After lowering substrate temperature to 600 degrees C, the hydrazine was introduced as a V group raw material on the 11th page of a silicon substrate from the gas installation tubing 2 made from a quartz, and trimethylgallium was introduced as 3 group raw materials after 1 minute. Installation of trimethylgallium was suspended after depositing the non-single crystal GaN layer 12 of 20nm of thickness. This was used as a buffer coat.

[0046] Subsequently, the temperature up of the substrate temperature was carried out to 1000 degrees C, in addition to the hydrazine, ammonia was introduced as a V group raw material, and trimethylgallium was introduced as 3 group raw materials after 1 minute. Installation of trimethylgallium was suspended after growing up the GaN layer 13 of 3 micrometers of thickness. When 3 micrometers grew, GaN layer 13 front face became flat, and propagation of the defect generated from the substrate interface was reduced remarkably. Subsequently, substrate temperature was lowered at 800 degrees C, trimethylgallium, trimethylaluminum, and trimethylindium were introduced into coincidence, and aluminum_{0.45}Ga_{0.5}In_{0.05}N layer 15 of 1.0 micrometers of thickness which carried out lattice matching to the GaN layer 13 was grown up. After suspending installation of trimethylgallium, trimethylaluminum, and trimethylindium, substrate temperature was lowered to 600 degrees C. Subsequently, as shown in the supply procedure of the material gas of drawing 6 (a), after it introduced trimethylindium and 1nm grew InN₂₂, trimethylindium was stopped, trimethylgallium and trimethylaluminum were introduced and 1nm AlGaIn₂₃ was grown up. Thus, it supplied alternately 30 times.

[0047] The false AlGaInN layer 24 by this was formed. After suspending installation of trimethylgallium and trimethylaluminum, the temperature up of the substrate temperature was carried out to 800 degrees C, trimethylgallium, trimethylaluminum, and trimethylindium were introduced into coincidence, and aluminum_{0.45}Ga_{0.5}In_{0.05}N layer 17 of 1.0 micrometers of thickness which carried out lattice matching to the GaN layer 13 was grown up again. After suspending installation of trimethylgallium, trimethylaluminum, and trimethylindium, installation of a hydrazine and ammonia was suspended in the place which lowered substrate temperature and became the temperature of 300 degrees C or less. After dropping the temperature of a substrate to a room temperature, the substrate was taken out from the inside of the coil 1 made from a quartz.

[0048] The front face of the obtained AlGaInN multilayers is a mirror plane, and checked strong

luminescence from the false AlGaInN layer 24 which consists of a strained layer superlattice of 22 layer of InN(s), and 23 layer of AlGaInN(s) as a result of photoluminescence measurement. By this invention, long luminescence with a wavelength of 500nm or more which did not have nothing profit until now was able to be obtained compared with the formation approach shown in a conventional approach and a conventional example 2.

[0049] In addition, the same result was obtained also in the formation approach shown in the material gas supply procedure of drawing 5 (b).

[0050] (Example 5) Cross-section structural drawing of the AlGaInN thin film produced by the formation approach of the AlGaInN thin film of the fifth example of this invention to drawing 7 is shown. About the formation approach of the AlGaInN thin film using the MOVPE equipment of drawing 1, order is explained later on.

[0051] (111) After carrying out organic washing of the field silicon substrate 11, it has arranged as a crystal growth substrate on the tray 6 made from a quartz, and introduced in the coil 1 made from a quartz. After introducing hydrogen gas in the coil 1 made from a quartz, coil 1 made from a quartz internal pressure was set as 1/10 atmospheric pressure, and the susceptor 4 made from graphite was rotated by 800 revolutions per minute. The temperature up of the susceptor 4 made from graphite was carried out to 1200 degrees C in hydrogen gas, and silicon substrate 11 front face was defecated. Methane was introduced and the carbonization layer 25 was formed in the substrate front face. After lowering substrate temperature to 600 degrees C, the hydrazine was introduced as a V group raw material on the 11th page of a silicon substrate from the gas installation tubing 2 made from a quartz, and trimethylgallium was introduced as 3 group raw materials after 1 minute. Installation of trimethylgallium was suspended after depositing the non-single crystal GaN layer 12 of 20nm of thickness. This was used as a buffer coat. Subsequently, the temperature up of the substrate temperature was carried out to 1000 degrees C, in addition to the hydrazine, ammonia was introduced as a V group raw material, and trimethylgallium was introduced as 3 group raw materials after 1 minute.

[0052] Installation of trimethylgallium was suspended after growing up the GaN layer 13 of 3 micrometers of thickness. When 3 micrometers grew, GaN layer 13 front face became flat, and propagation of the defect generated from the substrate interface was reduced remarkably. Subsequently, substrate temperature was lowered at 800 degrees C, trimethylgallium, trimethylaluminum, and trimethylindium were introduced into coincidence, and aluminum_{0.45}Ga_{0.5}In_{0.05}N layer 14 of 0.5 micrometers of thickness was grown up. After suspending installation of trimethylgallium, trimethylaluminum, and trimethylindium, installation of a hydrazine and ammonia was suspended in the place which lowered substrate temperature and became the temperature of 300 degrees C or less. After dropping the temperature of a substrate to a room temperature, the substrate was taken out from the inside of the coil 1 made from a quartz.

[0053] According to this invention, according to [in the obtained crystal front face] the hall effect in a mirror plane, carrier concentration is three or less [10^{15}cm^{-3}], and the GaN layer growth temperature grew up to be at 1000 degrees C though it was 800 degrees C and low temperature, and 4 yuan mixed crystal still more nearly quality than the case of an example 1 were obtained. Moreover, by carbonizing silicon substrate 11 front face, generating of the defect from a substrate interface was controlled remarkably, and the defect of about double [more] figures was reduced compared with the case of an example 1.

[0054] When silicon on sapphire was used for this formation approach, effectiveness was not accepted but, in the case of the silicon substrate, was completely very effective.

[0055] (Example 6) Cross-section structural drawing of the AlGaInN thin film produced by the formation approach of the AlGaInN thin film of the sixth example of this invention to drawing 8 is shown. About the formation approach of the AlGaInN thin film using the MOVPE equipment of drawing 1, order is explained later on.

[0056] (111) After carrying out organic washing of the field silicon substrate 11, it has arranged as a crystal growth substrate on the tray 6 made from a quartz, and introduced in the coil 1 made from a quartz. After introducing hydrogen gas in the coil 1 made from a quartz, coil 1 made from a quartz internal pressure was set as 1/10 atmospheric pressure, and the susceptor 4 made from graphite was rotated by 800 revolutions per minute. The temperature up of the susceptor 4 made from graphite was carried out to 1200 degrees C in hydrogen gas, and silicon substrate 11 front face was defecated. Methane was introduced and the carbonization layer 25 was formed in the substrate front face. Then, installation of methane was suspended, the hydrazine was introduced and the nitrated case 26 was formed on the carbonization layer 25. After lowering substrate temperature to 600 degrees C, the hydrazine was introduced as a V group raw

material on the 11th page of a silicon substrate from the gas installation tubing 2 made from a quartz, and trimethylgallium was introduced as 3 group raw materials after 1 minute. Installation of trimethylgallium was suspended after depositing the non-single crystal GaN layer 12 of 20nm of thickness. This was used as a buffer coat.

[0057] Subsequently, the temperature up of the substrate temperature was carried out to 1000 degrees C, in addition to the hydrazine, ammonia was introduced as a V group raw material, and trimethylgallium was introduced as 3 group raw materials after 1 minute. Installation of trimethylgallium was suspended after growing up the GaN layer 13 of 3 micrometers of thickness. When 3 micrometers grew, GaN layer 13 front face became flat, and propagation of the defect generated from the substrate interface was reduced remarkably. Subsequently, substrate temperature was lowered at 800 degrees C, trimethylgallium, trimethylaluminum, and trimethylindium were introduced into coincidence, and aluminum_{0.45}Ga_{0.5}In_{0.05}N layer 14 of 0.5 micrometers of thickness was grown up. After suspending installation of trimethylgallium, trimethylaluminum, and trimethylindium, installation of a hydrazine and ammonia was suspended in the place which lowered substrate temperature and became the temperature of 300 degrees C or less. After dropping the temperature of a substrate to a room temperature, the substrate was taken out from the inside of the coil 1 made from a quartz.

[0058] According to [in the crystal front face where it was obtained in the case of this example] the hall effect in a mirror plane, carrier concentration is three or less [10^{15}cm^{-3}], and the GaN layer growth temperature grew up to be at 1000 degrees C though it was 800 degrees C and low temperature, and 4 yuan mixed crystal still more nearly quality than the case of an example 1 were obtained. Moreover, generating of the defect from a substrate interface was remarkably controlled by carbonizing silicon substrate 11 front face. Moreover, since GaN carried out nuclear growth easily and precisely by nitriding a front face, even if compared with the case of an example 6, the defect was reduced further.

[0059] When silicon on sapphire was used for this formation approach, effectiveness was not accepted but, in the case of the silicon substrate, was completely very effective.

[0060] (Example 7) Cross-section structural drawing of the AlGaInN thin film produced by the formation approach of the AlGaInN thin film of the seventh example of this invention to drawing 9 is shown. About the formation approach of the AlGaInN thin film using the MOVPE equipment of drawing 1, order is explained later on.

[0061] (111) After carrying out organic washing of the field GaP substrate 27, it has arranged as a crystal growth substrate on the tray 6 made from a quartz, and introduced in the coil 1 made from a quartz. After introducing hydrogen gas in the coil 1 made from a quartz, coil 1 made from a quartz internal pressure was set as 1/10 atmospheric pressure, and the susceptor 4 made from graphite was rotated by 800 revolutions per minute. The temperature up of the susceptor 4 made from graphite was carried out to 800 degrees C in the phosphine ambient atmosphere, and GaP substrate 27 front face was defecated. Installation of a phosphine was suspended, the hydrazine was introduced and the nitrated case 28 was formed in the substrate front face. After lowering substrate temperature to 600 degrees C, trimethylgallium was introduced as 3 group raw materials on the 27th page of a GaP substrate from the gas installation tubing 2 made from a quartz. Installation of trimethylgallium was suspended after depositing the non-single crystal GaN layer 12 of 20nm of thickness. This was used as a buffer coat. Subsequently, the temperature up of the substrate temperature was carried out to 1000 degrees C, in addition to the hydrazine, ammonia was introduced as a V group raw material, and trimethylgallium was introduced as 3 group raw materials after 1 minute.

[0062] Installation of trimethylgallium was suspended after growing up the GaN layer 13 of 3 micrometers of thickness. When 3 micrometers grew, GaN layer 13 front face became flat, and propagation of the defect generated from the substrate interface was reduced remarkably. Subsequently, substrate temperature was lowered at 800 degrees C, trimethylgallium, trimethylaluminum, and trimethylindium were introduced into coincidence, and aluminum_{0.45}Ga_{0.5}In_{0.05}N layer 14 of 0.5 micrometers of thickness was grown up. After suspending installation of trimethylgallium, trimethylaluminum, and trimethylindium, installation of a hydrazine and ammonia was suspended in the place which lowered substrate temperature and became the temperature of 300 degrees C or less. After dropping the temperature of a substrate to a room temperature, the substrate was taken out from the inside of the coil 1 made from a quartz.

[0063] According to this invention, according to [in the obtained crystal front face] the hall effect in a mirror plane, although carrier concentration is three or less [10^{15}cm^{-3}] and used GaP for the substrate, the mixed crystal of 4 quality yuan comparable as AlGaInN formed on sapphire was obtained. moreover, by nitriding GaP substrate 27 front face, generating of the defect from a substrate interface was controlled

remarkably, and silicon on sapphire and a until [comparable] defect were reduced.

[0064] In the case of the GaP substrate, this formation approach was very effective. In addition, this invention is not limited to the example mentioned above. For example, the substrate to be used is not limited to an above-mentioned substrate. Moreover, the raw material used for crystal growth is not an above-mentioned limitation, either. The configuration of AlGaInN multilayers is not limited, either.

[0065]

[Effect of the Invention] Thus, according to this invention, since a substrate is rotated at high speed, using the mixed raw material of an alkylamine system, a hydrazine system or an alkylamine system, a hydrazine system, and ammonia as a nitrogen raw material, the AlGaInN thin film containing In with few point defects of a nitrogen hole etc. can be easily formed at low temperature.

[0066] Moreover, since the super-thin film multilayers which formed InN and AlGaInN by turns constitute an AlGaInN thin film, a more nearly quality AlGaInN thin film can be formed.

[0067] Moreover, since an AlGaInN strained layer superlattice structure is formed in advance of AlGaInN thin film formation, propagation of a rearrangement is reduced remarkably and a quality AlGaInN thin film can be formed.

[0068] Moreover, since a presentation forms the carbonization layer and nitrated case which change continuously in advance of non-single crystal layers, such as GaN, propagation of a rearrangement is reduced remarkably and quality AlGaInN can be formed also on substrates other than sapphire.

[0069] Therefore, it is very useful to the blue semiconductor laser component manufacture which can be used for high blue light emitting diode, the light source for information processors, etc. of luminous efficiency.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The schematic diagram of the MOVPE equipment explaining the formation approach of the example this invention

[Drawing 2] Cross-section structural drawing of the AlGaInN thin film by the formation approach of the AlGaInN thin film of the first example this invention

[Drawing 3] Cross-section structural drawing of the AlGaInN multilayers by the formation approach of the AlGaInN multilayers of the second example this invention

[Drawing 4] Cross-section structural drawing of the AlGaInN thin film by the formation approach of the AlGaInN thin film of the third example this invention

[Drawing 5] Cross-section structural drawing of the AlGaInN thin film by the formation approach of the AlGaInN multilayers of the fourth example this invention

[Drawing 6] The supply procedure Fig. of the material gas of the fourth example of this invention

[Drawing 7] Cross-section structural drawing of the AlGaInN thin film by the formation approach of the AlGaInN thin film of the fifth example this invention

[Drawing 8] Cross-section structural drawing of the AlGaInN thin film by the formation approach of the AlGaInN thin film of the sixth example this invention

[Drawing 9] Cross-section structural drawing of the AlGaInN thin film by the formation approach of the AlGaInN thin film of the seventh example this invention

[Description of Notations]

- 1 Coil made from Quartz
- 2 Gas Installation Tubing made from Quartz
- 3 Coil for High-frequency Heating
- 4 Susceptor made from Graphite
- 5 Susceptor Bearing Bar
- 6 Tray made from Quartz
- 7 Substrate
- 8 Exhaust Port
- 11 Silicon Substrate
- 12 Non-Single Crystal GaN Layer
- 13 21 GaN layer
- 14, 15, 17 aluminum $0.45\text{Ga}0.5\text{In}0.05\text{N}$ layer
- 16 19 Ga $0.8\text{In}0.2\text{N}$ layer
- 18 Aluminum $0.3\text{Ga}0.7\text{N}$ Layer
- 20 Aluminum $0.3\text{Ga}0.7\text{N}/\text{Ga}0.8\text{In}0.2\text{N}$ Strained Layer Superlattice
- 22 InN Layer
- 23 AlGaIn Layer
- 24 False AlGaInN Layer
- 25 Carbonization Layer
- 26 28 Nitrated case
- 27 GaP Substrate

[Translation done.]

*** NOTICES ***

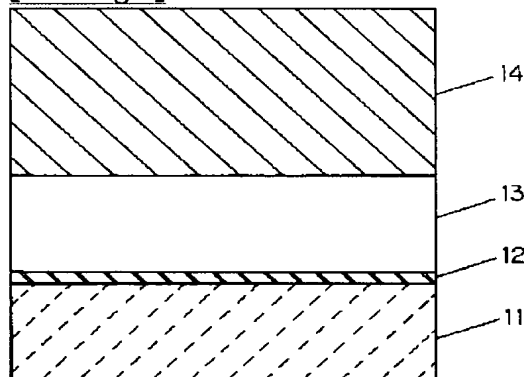
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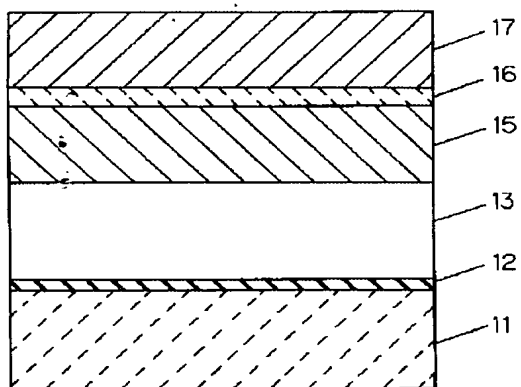
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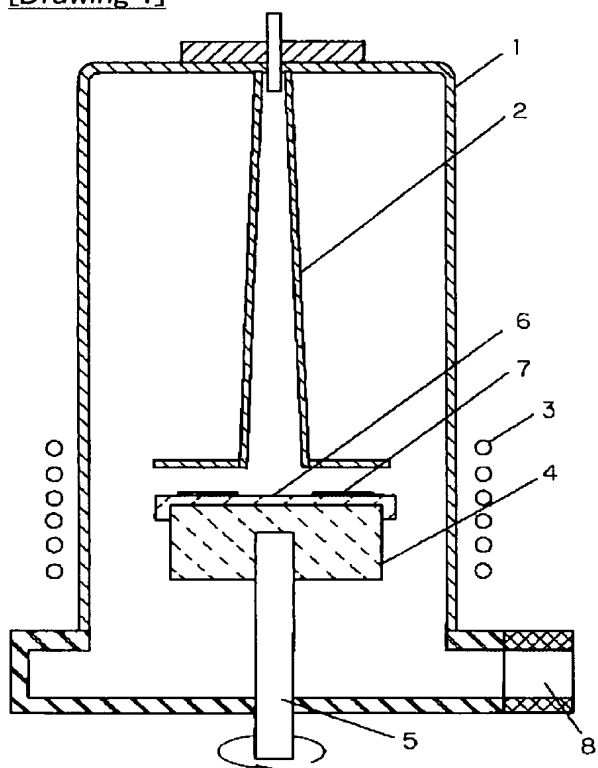
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DRAWINGS

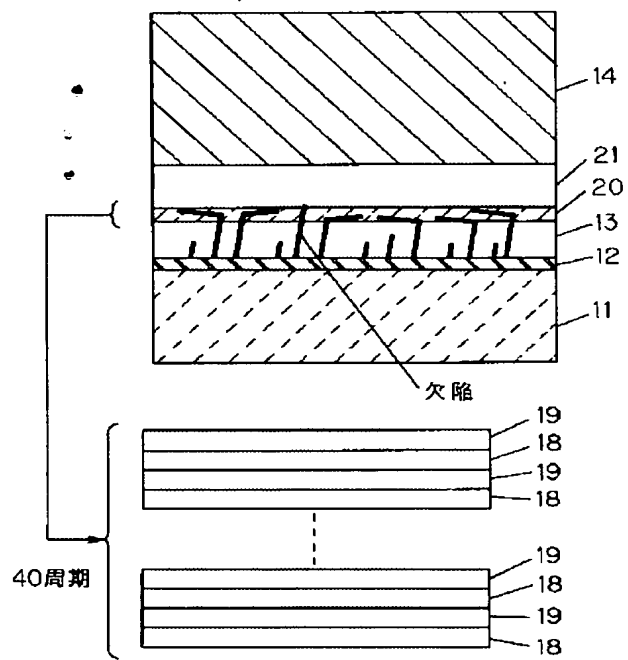
[Drawing 2]**[Drawing 3]**



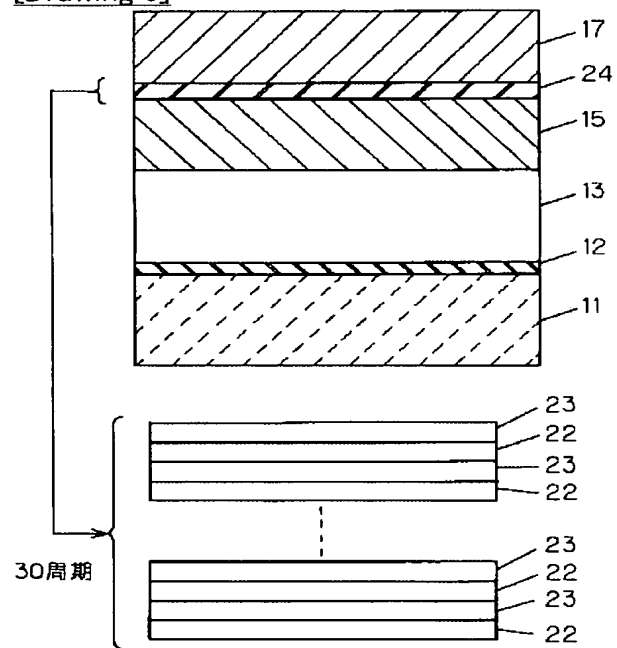
[Drawing 1]



[Drawing 4]

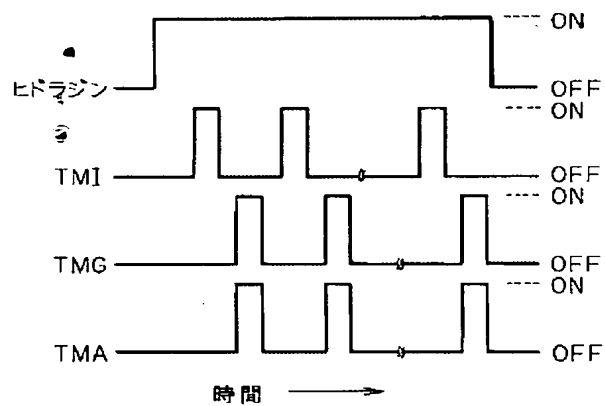


[Drawing 5]

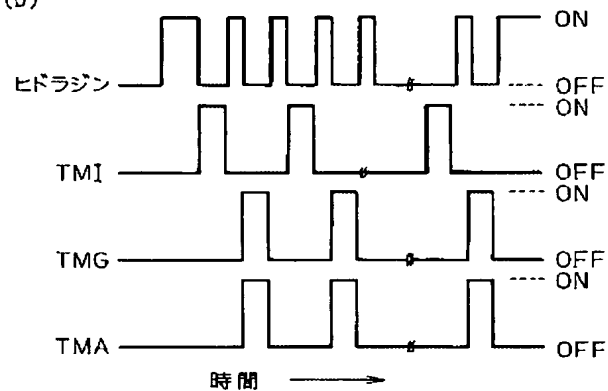


[Drawing 6]

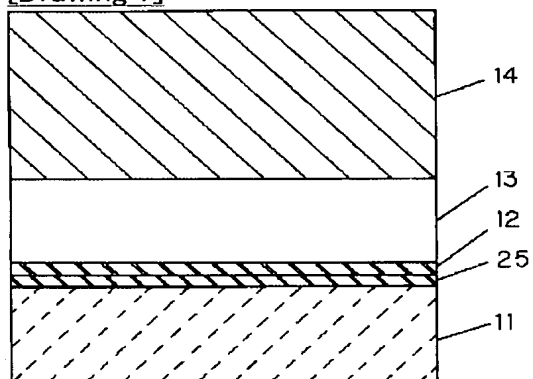
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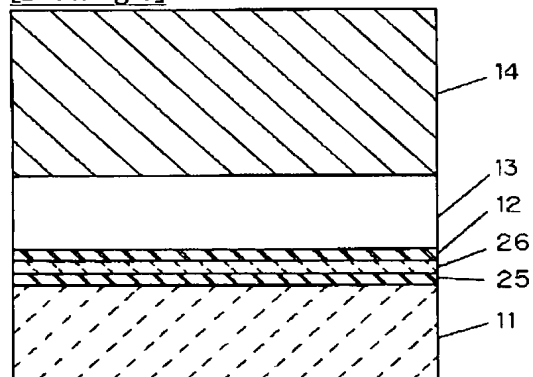
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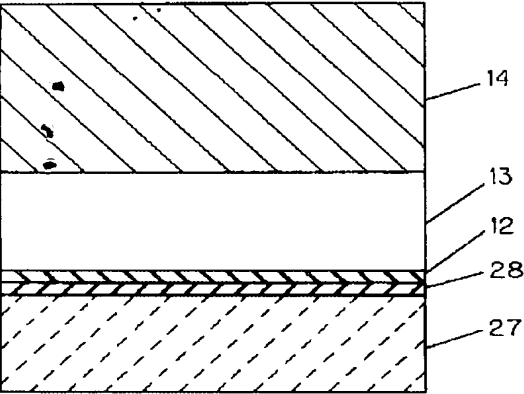
[Drawing 7]



[Drawing 8]



[Drawing 9]



[Translation done.]

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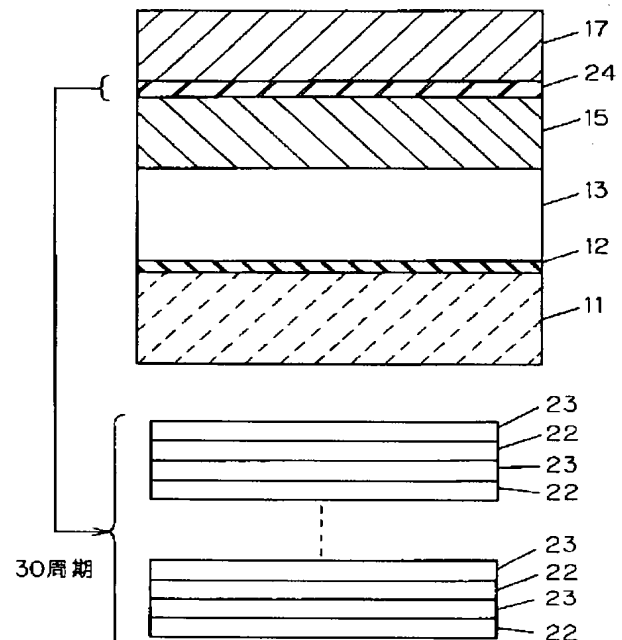
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(54)【発明の名称】 半導体薄膜の形成方法

(57)【要約】 (修正有)

【目的】 青色半導体レーザ素子製造に適した転位や点欠陥の少ない高品質なAlGaInN薄膜の形成方法を提供する。

【構成】 基板を配置した加熱体の回転速度が300回転/分以上とし、1200℃に加熱したSi基板11上にメタンガスを導入し、SiからSiCに連続的に変化する炭化層を形成する。600℃に低下させ、20nmのGaN非単結晶12を形成する。次いで、900℃以上の基板温度でGaN層13を形成し、前記GaN層上に300～900℃の範囲内に設定した基板温度で前記GaN層13に格子整合するAlGaInN層15を形成する。AlGaInN薄膜の形成はアルキルアミン系、ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を窒素原料とする。転位や点欠陥の少ない高品質なAlGaInN薄膜を低温で形成できる。



【特許請求の範囲】

【請求項1】加熱された基板表面上に3族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAlGaInN薄膜を形成する方法において、前記基板を配置した加熱体の回転速度が300回転/分以上であって、

900℃以上の基板温度でGaN層を形成し、前記GaN層上に300～900℃の範囲内に設定した基板温度でAlGaInN層を形成する方法であって、前記AlGaInN層の形成はアルキルアミン系、ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を窒素原料とすることを特徴とするAlGaInN薄膜の形成方法。

【請求項2】加熱された基板表面上に3族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介して $Al_{x_1}Ga_{y_1}In_{z_1}N$ 層/ $Al_{x_2}Ga_{y_2}In_{z_2}N$ 層/ $Al_{x_3}Ga_{y_3}In_{z_3}N$ 層 ($E_{g_2} < E_{g_1}$ 、 $E_{g_3} : E_{g_1}$ はバンドギャップ) からなるAlGaInN多層膜を形成する方法において、

前記基板を配置した加熱体の回転速度が300回転/分以上であって、900℃以上の基板温度でGaN層を形成し、前記GaN層上に300～900℃の範囲内に設定した基板温度で前記GaN層に格子整合する $Al_{x_1}Ga_{y_1}In_{z_1}N$ 層と2%以下の格子不整合する $Al_{x_2}Ga_{y_2}In_{z_2}N$ 層と前記GaN層に格子整合する $Al_{x_3}Ga_{y_3}In_{z_3}N$ 層を形成する方法であって、前記AlGaInN多層膜の形成はアルキルアミン系、ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を窒素原料とすることを特徴とするAlGaInN多層膜の形成方法。

【請求項3】加熱された基板表面上に3族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してGaN層を形成し、前記GaN層上にAlGaInN薄膜を形成する方法において、前記基板を配置した加熱体の回転速度が300回転/分以上であって、前記GaN層中もしくはGaN層上にAlGaInN層からなる歪超格子構造を配置することを特徴とするAlGaInN薄膜の形成方法。

【請求項4】AlGaInN層は3族構成元素を含む原料の供給を間欠的に行い、InN層とAlGaN層を構成する原料の繰り返し供給により形成することを特徴とする請求項第1、3記載のAlGaInN薄膜の形成方法及び第2記載のAlGaInN多層膜の形成方法。

【請求項5】加熱された基板表面上に3族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAlGaInN薄膜を形成する方法において、水素ガスと炭素を含む原料の雰囲気中で前記基板を加熱し前記基板表面上に形成した炭化層を緩衝層とすることを特徴とするAlGaInN薄膜の形成方法。

【請求項6】加熱された基板表面上に3族構成元素を含

む原料および窒素を含む原料を供給して緩衝層を介してAlGaInN薄膜を形成する方法において、炭素を含む原料の雰囲気中で前記基板を加熱し前記基板表面上に形成した炭化層と次いでアルキルアミン系、ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を含む雰囲気中で前記炭化層表面上に形成した窒化層を少なくとも緩衝層とすることを特徴とするAlGaInN薄膜の形成方法。

【請求項7】加熱された基板表面上に3族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAlGaInN薄膜を形成する方法において、アルキルアミン系、ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を含む雰囲気中で前記基板表面上に形成した窒化層と次いで3族構成元素を含む原料とアルキルアミン系、ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を含む雰囲気中で前記窒化層表面上に形成したGaN非単結晶層を緩衝層とすることを特徴とするAlGaInN薄膜の形成方法。

【請求項8】基板を配置した加熱体の回転速度を300回転/分以上とすることを特徴とする請求項第5～7のいずれかに記載のAlGaInN薄膜の製造方法。

【請求項9】基板がサファイア、SiC、ZnO、Si、GaAs、GaP、InPであることを特徴とする請求項第1、3、4、5、6、7のいずれかに記載のAlGaInN薄膜の形成方法。

【請求項10】基板がサファイア、SiC、ZnO、Si、GaAs、GaP、InPであることを特徴とする請求項2記載のAlGaInN多層膜の形成方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】この発明は、緑・青色発光ダイオードや光ディスク等情報処理装置用光源に用いることのできる青色もしくは更に短波長の半導体レーザー素子の製造方法に関するもので、窒化物系材料の薄膜形成方法に係わるものである。

【0002】

【従来の技術】1988年に670nm帯AlGaInP系赤色半導体レーザーが商品化されて以来、レーザープリンター、光ディスク等の情報処理装置用光源として短波長半導体レーザーの開発が活発に行われている。開発の中心は当初670～690nmであったが、バーコードリーダーの視認性の改善、光ディスクの高密度化等の要求にともなって、波長領域はHe-Neガスレーザーと同レベルの630nm帯へと移行しつつある。さらに将来、記憶容量の増大に伴って、赤色より短波長の青・緑色から紫外域にわたった半導体レーザー実現が切望されており、p型導電型制御が可能となったことを契機に2-6族系半導体レーザーの研究が急速に進展してきている。一方、窒化ガリウム(GaN)は、約3.4eVの広エネルギー

ギャップを持つ直接遷移型の化合物半導体で青色から紫外領域にわたる発光素子として有望な材料であるがGaNバルク基板結晶が容易に作製できず、ほかに良質な基板結晶がないことから半導体レーザとしての開発はあまり進展していなかった。

【0003】GaN薄膜の作製方法としては、 α -Al₂O₃（サファイア）基板上にMOVPE法（有機金属気相成長法）により気相成長する方法が一般的に用いられている。これは、例えばトリメチルガリウムとアンモニアを1050℃程度に加熱した基板、例えば、サファイア表面上で分解、反応させ、GaN薄膜を成長しようとするものである。最近サファイアの（0001）C面を用い、GaNやAlN非単結晶層を介して比較的良質のGaN薄膜を形成できることが実証された。しかし、サファイアC面とGaNとの間には13.8%という極めて大きな格子不整合や大きな熱膨張係数の差があるので、非単結晶層を介した場合においては格子不整合の緩和は効率的におこるものの依然として10⁸cm⁻²以上のミスフィット転位が存在し高品質な薄膜形成ができなかった。

【0004】Al、Inを含むAlGaInN四元混晶薄膜を結晶成長する上での問題点は、上述のように格子整合する良質な基板結晶が存在しないことのほかは、窒素原料として用いられるアンモニアの分解効率が低いこと、及びAlN、GaNの成長温度に比較してInNの分解温度がそれらよりも低温であることに集約される。

【0005】アンモニアの分解には高温を要するため、上述のように基板温度を900～1100℃にする必要があった。このため、膜中に多数の窒素の空孔が生じ、成長したGaN層はそのままではn型伝導性を示す薄膜となってしまう、高抵抗のGaN薄膜が得られにくいという欠点があった。したがって、3族と5族の供給比、いわゆる3/5比を1000から5000と他の材料系に比べて1桁から2桁大きくする必要があった。できるだけ低温で成長を行うことが望ましいが、アンモニアは分解温度が非常に高いので、低温で成長を行う場合でも、極めて大量のアンモニアが必要であり、実用的に供給できる範囲を超えていた。

【0006】また、アンモニアを用いて1000℃程度でAlGaInNの成長を行った場合、アンモニアは分解効率が低いため、Inは基板表面から脱離しやすい。InNの分解によってInの取り込み量が著しく少ないため、組成の制御が困難で、表面のモロロジーの劣化をもたらし、高品質のAlGaInN薄膜が得られにくいという欠点があった。

【0007】

【発明が解決しようとする課題】上述の従来技術によれば、窒化膜の結晶成長には、その窒素の原料としてアンモニアを用いたため、比較的低温度で成長を行うことができなかった。したがって、MOVPE成長時に、基板

上で大きな熱対流が発生し、基板上への均一な原料供給が困難であり、不純物ドーピングによる伝導型の制御、すなわちp型伝導の窒化膜の成長も困難であった。本発明は、低温で制御性に優れた結晶成長を可能にして、窒素の空孔が少ない良質のAlGaInN薄膜を得ることが可能で、不純物ドーピングにより容易にn型伝導型ないしはp型伝導性にし得る伝導型制御の可能なAlGaInN薄膜の形成方法を提供することを目的とする。特にInを含むAlGaInN薄膜の形成方法を提供することを主な目的としている。

【0008】また従来技術によれば、窒化膜とサファイア基板の格子定数の整合性は悪く、また、熱膨張係数の差も大きいため、成長した窒化膜にはビットやクラックが入りやすく、均一で平坦性のよい窒化膜の成長が困難であった。

【0009】本発明は、従来より低温で薄膜形成でき、転位が少なく平坦性のよいAlGaInN薄膜の形成方法を提供することを目的とする。

【0010】さらに従来技術によれば、サファイアが基板として用いられていたが、加工が困難でデバイスの作製が容易ではなかった。本発明は、安価で加工の容易な基板上に均一で平坦性のよいAlGaInN薄膜の形成方法を提供することを目的とする。

【0011】

【課題を解決するための手段】上記目的を達成するために、請求項1記載のAlGaInN薄膜の形成方法は、加熱された基板表面上に3族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAlGaInN薄膜を形成する方法において、前記基板を配置した加熱体の回転速度が300回転/分以上であって、900℃以上の基板温度でGaN層を形成し、前記GaN層上に300～900℃の範囲内に設定した基板温度でAlGaInN層を形成する方法であって、前記AlGaInN層の形成はアルキルアミン系、ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を窒素原料とすることを特徴とする。

【0012】請求項2記載のAlGaInN多層膜の作製方法は、加熱された基板表面上に3族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAl_{1-x1}Ga_{x1}In_{z1}N層/Al_{1-x2}Ga_{x2}In_{z2}N層/Al_{1-x3}Ga_{x3}In_{z3}N層（E_{g2}<E_{g1}、E_{g3}：E_gはバンドギャップ）からなるAlGaInN多層膜を形成する方法において、前記基板を配置した加熱体の回転速度が300回転/分以上であって、900℃以上の基板温度でGaN層を形成し、前記GaN層上に300～900℃の範囲内に設定した基板温度で前記GaN層に格子整合するAl_{1-x1}Ga_{x1}In_{z1}N層と2%以下の格子不整合するAl_{1-x2}Ga_{x2}In_{z2}N層と前記GaN層に格子整合するAl_{1-x3}Ga_{x3}In_{z3}N層を形成する方法であって、前記AlGaInN多層膜の形成はアルキルアミン系、

ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を窒素原料とすることを特徴とする。

【0013】請求項4記載のAlGaInN薄膜及び多層膜の作製方法は、請求項第1、3記載のAlGaInN薄膜の形成方法及び第2記載のAlGaInN多層膜の形成方法において、AlGaInN層は3族構成元素を含む原料の供給を間欠的にを行い、InN層とAlGaInN層を構成する原料の繰り返し供給により形成することとを特徴とする。

【0014】請求項3記載のAlGaInN薄膜の形成方法は、加熱された基板表面上に3族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してGaInN層を形成し、前記GaInN層上にAlGaInN薄膜を形成する方法において、前記基板を配置した加熱体の回転速度が300回転/分以上であって、前記GaInN層中もしくはGaInN層上にAlGaInN層からなる歪超格子構造を配置することを特徴とする。

【0015】請求項5記載のAlGaInN薄膜の形成方法は、加熱された基板表面上に3族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAlGaInN薄膜を形成する方法において、水素ガスと炭素を含む原料の雰囲気中で前記基板を加熱し前記基板表面上に形成した炭化層を緩衝層とすることを特徴とする。

【0016】請求項6記載のAlGaInN薄膜の形成方法は、加熱された基板表面上に3族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAlGaInN薄膜を形成する方法において、炭素を含む原料の雰囲気中で前記基板を加熱し前記基板表面上に形成した炭化層と次いでアルキルアミン系、ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を含む雰囲気中で前記炭化層表面上に形成した窒化層を少なくとも緩衝層とすることを特徴とする。

【0017】請求項7記載のAlGaInN薄膜の形成方法は、加熱された基板表面上に3族構成元素を含む原料および窒素を含む原料を供給して緩衝層を介してAlGaInN薄膜を形成する方法において、アルキルアミン系、ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を含む雰囲気中で前記基板表面上に形成した窒化層と次いで3族構成元素を含む原料とアルキルアミン系、ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を含む雰囲気中で前記窒化層表面上に形成したGaInN非単結晶層を緩衝層とすることを特徴とする。

【0018】以上の請求項において、基板を配置した加熱体の回転速度は300回転/分以上とすることが望ましい。また、基板はサファイア、SiC、ZnO、Si、GaAs、GaP、InPであることが望ましい。

【0019】

【作用】AlGaInN薄膜の結晶成長における問題点の一つは、AlN、GaInNの成長温度に比較してInNの分解温度がそれよりも低温であることである。すなわち、アンモニアを用いて、AlGaInN薄膜の成長温度でAlGaInN薄膜の成長を行った場合、アンモニアは分解効率が低いため、Inは基板表面から脱離しやすい。InNの分解によってInの取り込み量が著しく少ないため、組成の制御が困難で、表面のモロロジーの劣化をもたらす。

10 【0020】請求項1のAlGaInN薄膜の作製方法、請求項2のAlGaInN多層膜の作製方法によれば、分解温度の低いアルキルアミン系、ヒドラジン系を少なくとも含む窒素原料を用い、基板を高速回転させたので、比較的低温で成長でき、成長温度が高いことによるガス対流の抑制、Inの解離の抑制が可能となる。よって従来よりも低温で高品質なAlGaInN薄膜もしくはAlGaInN多層膜の形成が可能となる。

20 【0021】請求項3のAlGaInN薄膜の作製方法によれば、アルキルアミン系、ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を含む窒素原料を用いて低温で例えばIn、N/N/Ga、Al、N/Nのように原料ガスを交互に基板上に供給することにより、窒素空孔が少なくInの取り込まれが安定となるため、従来よりも低温で高品質なAlGaInN薄膜もしくはAlGaInN多層膜の形成が可能となる。

30 【0022】AlGaInN薄膜の結晶成長における問題点の一つは、格子整合基板がないことである。従来は、サファイア基板上にAlNやGaInNの非単結晶層を介して窒化物薄膜の形成を行っていたが、サファイア基板は加工が困難で半導体素子用基板としては不向きである。しかも、AlNやGaInN非単結晶層との間には、依然として大きな格子不整合や熱歪みが存在しているため、基板との界面で発生した転位の伝搬を十分抑制することはできない。

40 【0023】請求項4のAlGaInN薄膜の作製方法によれば、AlGaInN薄膜形成する前に歪みを含むAlGaInN超格子を配置するので、基板界面から発生した転位は面内方向への運動成分が大きくなるため、上部層への伝搬を効率的に抑制でき高品質なAlGaInN薄膜を形成できる。

50 【0024】請求項5、6のAlGaInN薄膜の作製方法によれば、例えばシリコン基板上にAlGaInN薄膜を形成する前に行う熱処理中に基板内に炭素が拡散し、基板内からシリコンが解離することにより、シリコンからSiCへと連続的な組成変化をする炭化層を形成できる。SiCの格子定数は窒化物の格子定数と近いいため、転位の発生が抑制され、また熱歪みの緩和にも効果があるため、AlGaInN薄膜への転位の伝搬を大幅に低減できる。

【0025】請求項7のAlGaInN薄膜の作製方法によれば、例えばGaP基板上にAlGaInN薄膜を形成する前に行う熱処理中に基板内に窒素が拡散し、基板内からPが解離することにより、GaPからGaNへと連続的な組成変化をする窒化層を形成できる。さらに、GaNの非単結晶層を形成するので、均一かつ粒径のそろった核を形成できる。このため転位の発生が抑制され、また熱歪みの緩和にも効果があるため、AlGaInN薄膜への転位の伝搬を大幅に低減できる。

【0026】このようにサファイアをはじめ、それ以外の加工の容易な基板、例えばシリコン基板やGaP基板上にも高品質なAlGaInN薄膜の形成が可能である。

【0027】したがって、本発明は発光効率の高い青色発光ダイオードや情報処理装置用光源などに用いることのできる青色半導体レーザ素子製造に極めて有用である。

【0028】

【実施例】以下、実施例で本発明を説明する。なお、以下同一部分については同一符号を記す。

【0029】AlGaInN薄膜の製造には、図1に概略的に示すMOVPE装置を用いた。ここで、石英製反応管1の内部には石英製ガス導入管2が取り付けられている。石英製ガス導入管からは3族構成元素を含む原料および窒素を含む原料を同時に供給できるようになっている。石英製反応管1の外周には高周波加熱用コイル3が設置され、また、内部にはSiCコートされたグラファイト製サセプター4が設置されている。グラファイト製サセプター4はモーターによって1000回転/分程度に回転可能なサセプター支持棒5により支持されている。グラファイト製サセプター4上面には、石英製トレー6上に搭載された基板7が設置できるような構成となっている。また、石英製反応管1の底部には真空ポンプに接続された排気口8が設けられていて、石英製反応管1内の圧力調整及びガスの排気ができるようになっている。

【0030】（実施例1）図2に本発明の第一の実施例のAlGaInN薄膜の形成方法により作製したAlGaInN薄膜の断面構造図を示す。図1のMOVPE装置を用いたAlGaInN薄膜の形成方法について、順を追って説明する。

【0031】（111）面シリコン基板11を有機洗浄した後、石英製トレー6上に結晶成長基板として配置し、石英製反応管1内に導入した。石英製反応管1内に水素ガスを導入した後、石英製反応管1内圧力を1/10気圧に設定し、グラファイト製サセプター4を800回転/分で回転させた。水素ガス中でグラファイト製サセプター4を1200℃まで昇温し、シリコン基板11表面の清浄化を行った。基板温度を600℃まで降温した後、石英製ガス導入管2からシリコン基板11面上に

V族原料としてヒドラジンを導入し、1分後に3族原料としてトリメチルガリウムを導入した。膜厚20nmの非単結晶GaN層12を堆積した後、トリメチルガリウムの導入を停止した。これを緩衝層として用いた。次いで、基板温度を1000℃に昇温し、V族原料としてヒドラジンに加えてアンモニアを導入し、1分後に3族原料としてトリメチルガリウムを導入した。膜厚3μmのGaN層13を成長した後、トリメチルガリウムの導入を停止した。3μm成長すると、GaN層13表面は平坦となり、基板界面から発生した欠陥の伝搬は著しく低減された。次いで、基板温度を800℃に降温し、トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムを同時に導入し、膜厚0.5μmのAl_{0.45}Ga_{0.55}In_{0.0}N層14を成長した。トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムの導入を停止した後、基板温度を降温し300℃以下の温度になったところでヒドラジンとアンモニアの導入を停止した。基板の温度を室温まで降下させた後、石英製反応管1内より基板を取り出した。

【0032】グラファイト製サセプター4を10回転/分で回転させた場合は、石英製ガス導入管2に多量の反応生成物が付着し、得られた結晶表面は凸凹で四元混晶層のIn組成が0.02であったのに対し、本実施例の場合は、石英製ガス導入管2への反応生成物の付着は少なく、鏡面でホール効果によるとキャリア濃度は 10^{15} cm^{-3} と極めて欠陥の少ない四元混晶が得られた。また、In組成は0.05となり、800回転/分の高速回転によりInの取り込まれ率が増大することを確認した。800℃と低温でありながら、1000℃で成長したGaN層より高品質な四元混晶が得られた。これらの結果は、ヒドラジンとアンモニアを同時に導入したことによる窒素空孔の低減及びInの解離の抑制効果であり、高速回転によるガス流の対流抑制及び原料の効率的な取り込まれによると考えられる。

【0033】（実施例2）図3に本発明の第二の実施例のAlGaInN多層膜の形成方法により作製したAlGaInN多層膜の断面構造図である。図1のMOVPE装置を用いたAlGaInN多層膜の形成方法について、順を追って説明する。

【0034】（111）面シリコン基板11を有機洗浄した後、石英製トレー6上に結晶成長基板として配置し、石英製反応管1内に導入した。石英製反応管1内に水素ガスを導入した後、石英製反応管1内圧力を1/10気圧に設定し、グラファイト製サセプター4を800回転/分で回転させた。水素ガス中でグラファイト製サセプター4を1200℃まで昇温し、シリコン基板11表面の清浄化を行った。基板温度を600℃まで降温した後、石英製ガス導入管2からシリコン基板11面上にV族原料としてヒドラジンを導入し、1分後に3族原料としてトリメチルガリウムを導入した。

【0035】膜厚20nmの非単結晶Ga_{0.4}N層12を堆積した後、トリメチルガリウムの導入を停止した。これを緩衝層として用いた。次いで、基板温度を1000℃に昇温し、V族原料としてヒドラジンに加えてアンモニアを導入し、1分後に3族原料としてトリメチルガリウムを導入した。膜厚3μmのGa_{0.4}N層13を成長した後、トリメチルガリウムの導入を停止した。

【0036】3μm成長すると、Ga_{0.4}N層13表面は平坦となり、基板界面から発生した欠陥の伝搬は著しく低減された。次いで、基板温度を800℃に降温し、トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムを同時に導入し、Ga_{0.4}N層13に格子整合した膜厚1.0μmのAl_{0.4}Ga_{0.6}In_{0.2}N層15を成長した。トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムの導入を停止した後、基板温度を700℃まで降温し、トリメチルガリウムとトリメチルインジウムを同時に導入し、格子不整をもつ膜厚0.01μmのGa_{0.4}In_{0.2}N層16を成長した。次いで、トリメチルガリウムとトリメチルインジウムの導入を停止した後、基板温度を800℃まで昇温し、トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムを同時に導入し、Ga_{0.4}N層13に格子整合した膜厚1.0μmのAl_{0.4}Ga_{0.6}In_{0.2}N層17を再度成長した。トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムの導入を停止した後、基板温度を降温し300℃以下の温度になったところでヒドラジンとアンモニアの導入を停止した。基板の温度を室温まで降下させた後、石英製反応管1内より基板を取り出した。

【0037】得られたAlGaInN多層膜の表面は鏡面であり、フォトルミネッセンス測定の結果、Ga_{0.4}In_{0.2}N層16からの強い発光を確認した。

【0038】グラファイト製サセプター4を10回転/分で回転させた場合は、石英製ガス導入管2に多量の反応生成物が付着し、得られた結晶表面は凸凹でGaInN層のIn組成が0.12であったのに対し、本実施例の場合は、石英製ガス導入管2への反応生成物の付着は少なく、In組成は0.2となり800回転/分の回転によりInの取り込まれ率の増大を確認した。800℃と低温でありながら、1000℃で成長したGa_{0.4}Nより高品質なInを含む多層膜が得られた。これらの結果は、ヒドラジンとアンモニアを同時に導入したことによる窒素空孔の低減及びInの解離の抑制効果であり、高速回転によるガス流の対流抑制及び原料の効率的な取り込まれによると考えられる。

【0039】また、格子不整のあるGaInNを導入しても格子整合混晶と同程度の結晶性を維持しながら、多層膜の形成が可能であった。

【0040】(実施例3)図4に本発明の第三の実施例のAlGaInN薄膜の形成方法により作製したAlG

aInN薄膜の断面構造図を示す。図1のMOVPE装置を用いたAlGaInN薄膜の製造方法について、順を追って説明する。

【0041】(111)面シリコン基板11を有機洗浄した後、石英製トレー6上に結晶成長基板として配置し、石英製反応管1内に導入した。石英製反応管1内に水素ガスを導入した後、石英製反応管1内圧力を1/10気圧に設定し、グラファイト製サセプター4を800回転/分で回転させた。水素ガス中でグラファイト製サセプター4を1200℃まで昇温し、シリコン基板11表面の清浄化を行った。基板温度を600℃まで降温した後、石英製ガス導入管2からシリコン基板11面上にV族原料としてヒドラジンを導入し、1分後に3族原料としてトリメチルガリウムを導入した。膜厚20nmの非単結晶Ga_{0.4}N層12を堆積した後、トリメチルガリウムの導入を停止した。これを緩衝層として用いた。

【0042】次いで、基板温度を1000℃に昇温し、V族原料としてヒドラジンに加えてアンモニアを導入し、1分後に3族原料としてトリメチルガリウムを導入した。膜厚3μmのGa_{0.4}N層13を成長した後、トリメチルガリウムの導入を停止した。3μm成長すると、Ga_{0.4}N層13表面は平坦となり、基板界面から発生した欠陥の伝搬は著しく低減された。次いで、基板温度を800℃に降温し、トリメチルガリウムとトリメチルアルミニウムを同時に導入し、膜厚2nmのAl_{0.4}Ga_{0.6}N層18を成長した。トリメチルガリウムとトリメチルアルミニウムの導入を停止した後、トリメチルガリウムとトリメチルインジウムを同時に導入し、膜厚2nmのGa_{0.4}In_{0.2}N層19を成長した。連続して40周期のAl_{0.4}Ga_{0.6}N/Ga_{0.4}In_{0.2}N歪超格子20を成長した後、再度トリメチルガリウムを導入し膜厚2μmのGa_{0.4}N層21を成長してトリメチルガリウムの導入を停止した。次いで、トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムを同時に導入し、膜厚0.5μmのAl_{0.4}Ga_{0.6}In_{0.2}N層14を成長した。トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムの導入を停止した後、基板温度を降温し300℃以下の温度になったところでヒドラジンとアンモニアの導入を停止した。基板の温度を室温まで降下させた後、石英製反応管1内より基板を取り出した。

【0043】Al_{0.4}Ga_{0.6}N/Ga_{0.4}In_{0.2}N歪超格子20を導入することによって基板界面から発生した欠陥の伝搬は著しく抑制され、実施例1の場合に比べてさらに2桁程度の欠陥が低減された。得られた結晶表面は鏡面でホール効果によるとキャリア濃度は10¹⁵cm⁻³以下であり、成長温度が800℃と低温でありながら1000℃で成長したGa_{0.4}N層、さらには実施例1の場合よりもより高品質な四元混晶が得られた。

【0044】(実施例4)図5に本発明の第四の実施例

のAlGaInN多層膜の形成方法により作製したAlGaInN多層膜の断面構造図である。図1のMOVPE装置を用いたAlGaInN多層膜の形成方法について、順を追って説明する。

【0045】(111)面シリコン基板11を有機洗浄した後、石英製トレー6上に結晶成長基板として配置し、石英製反応管1内に導入した。石英製反応管1内に水素ガスを導入した後、石英製反応管1内圧力を1/10気圧に設定し、グラファイト製セプター4を800回転/分で回転させた。水素ガス中でグラファイト製セプター4を1200℃まで昇温し、シリコン基板11表面の清浄化を行った。基板温度を600℃まで降温した後、石英製ガス導入管2からシリコン基板11面上にV族原料としてヒドラジンを導入し、1分後に3族原料としてトリメチルガリウムを導入した。膜厚20nmの非単結晶GaN層12を堆積した後、トリメチルガリウムの導入を停止した。これを緩衝層として用いた。

【0046】次いで、基板温度を1000℃に昇温し、V族原料としてヒドラジンに加えてアンモニアを導入し、1分後に3族原料としてトリメチルガリウムを導入した。膜厚3μmのGaN層13を成長した後、トリメチルガリウムの導入を停止した。3μm成長すると、GaN層13表面は平坦となり、基板界面から発生した欠陥の伝搬は著しく低減された。次いで、基板温度を800℃に降温し、トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムを同時に導入し、GaN層13に格子整合した膜厚1.0μmのAl_{0.45}Ga_{0.55}In_{0.05}N層15を成長した。トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムの導入を停止した後、基板温度を600℃まで降温した。次いで、図6(a)の原料ガスの供給手順に示すように、トリメチルインジウムを導入しInN22を1nm成長した後、トリメチルインジウムを停止し、トリメチルガリウムとトリメチルアルミニウムを導入し、1nmのAlGaInN23を成長した。このようにして30回交互に供給した。

【0047】これにより疑似的なAlGaInN層24を形成した。トリメチルガリウムとトリメチルアルミニウムの導入を停止した後、基板温度を800℃まで昇温し、トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムを同時に導入し、GaN層13に格子整合した膜厚1.0μmのAl_{0.45}Ga_{0.55}In_{0.05}N層17を再度成長した。トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムの導入を停止した後、基板温度を降温し300℃以下の温度になったところでヒドラジンとアンモニアの導入を停止した。基板の温度を室温まで降下させた後、石英製反応管1内より基板を取り出した。

【0048】得られたAlGaInN多層膜の表面は鏡面であり、フォトルミネッセンス測定の結果、InN2

2層とAlGaInN23層の歪超格子からなる疑似的なAlGaInN層24からの強い発光を確認した。本発明により、従来の方法や実施例2に示す形成方法に比べて、今までになし得なかった500nm以上の波長の長い発光を得ることができた。

【0049】なお、図5(b)の原料ガス供給手順に示す形成方法においても、同様な結果が得られた。

【0050】(実施例5) 図7に本発明の第五の実施例のAlGaInN薄膜の形成方法により作製したAlGaInN薄膜の断面構造図を示す。図1のMOVPE装置を用いたAlGaInN薄膜の形成方法について、順を追って説明する。

【0051】(111)面シリコン基板11を有機洗浄した後、石英製トレー6上に結晶成長基板として配置し、石英製反応管1内に導入した。石英製反応管1内に水素ガスを導入した後、石英製反応管1内圧力を1/10気圧に設定し、グラファイト製セプター4を800回転/分で回転させた。水素ガス中でグラファイト製セプター4を1200℃まで昇温し、シリコン基板11表面の清浄化を行った。メタンガスを導入し基板表面に炭化層25を形成した。基板温度を600℃まで降温した後、石英製ガス導入管2からシリコン基板11面上にV族原料としてヒドラジンを導入し、1分後に3族原料としてトリメチルガリウムを導入した。膜厚20nmの非単結晶GaN層12を堆積した後、トリメチルガリウムの導入を停止した。これを緩衝層として用いた。次いで、基板温度を1000℃に昇温し、V族原料としてヒドラジンに加えてアンモニアを導入し、1分後に3族原料としてトリメチルガリウムを導入した。

【0052】膜厚3μmのGaN層13を成長した後、トリメチルガリウムの導入を停止した。3μm成長すると、GaN層13表面は平坦となり、基板界面から発生した欠陥の伝搬は著しく低減された。次いで、基板温度を800℃に降温し、トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムを同時に導入し、膜厚0.5μmのAl_{0.45}Ga_{0.55}In_{0.05}N層14を成長した。トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムの導入を停止した後、基板温度を降温し300℃以下の温度になったところでヒドラジンとアンモニアの導入を停止した。基板の温度を室温まで降下させた後、石英製反応管1内より基板を取り出した。

【0053】本発明によれば、得られた結晶表面は鏡面でホール効果によるとキャリア濃度は10¹⁵cm⁻³以下であり、成長温度が800℃と低温でありながら1000℃で成長したGaN層、さらには実施例1の場合よりもより高品質な四元混晶が得られた。また、シリコン基板11表面を炭化することにより、基板界面からの欠陥の発生は著しく抑制され、実施例1の場合に比べてさらに2桁程度の欠陥が低減された。

【0054】この形成方法は、サファイア基板を用いた場合には全く効果は認められず、シリコン基板の場合に極めて有効であった。

【0055】（実施例6）図8に本発明の第六の実施例のAlGaInN薄膜の形成方法により作製したAlGaInN薄膜の断面構造図を示す。図1のMOVPE装置を用いたAlGaInN薄膜の形成方法について、順を追って説明する。

【0056】（111）面シリコン基板11を有機洗浄した後、石英製トレー6上に結晶成長基板として配置し、石英製反応管1内に導入した。石英製反応管1内に水素ガスを導入した後、石英製反応管1内圧力を1/10気圧に設定し、グラファイト製サセプター4を800回転/分で回転させた。水素ガス中でグラファイト製サセプター4を1200℃まで昇温し、シリコン基板11表面の清浄化を行った。メタンガスを導入し基板表面に炭化層25を形成した。その後、メタンガスの導入を停止し、ヒドラジンを導入し炭化層25上に窒化層26を形成した。基板温度を600℃まで降温した後、石英製ガス導入管2からシリコン基板11面上にV族原料としてヒドラジンを導入し、1分後に3族原料としてトリメチルガリウムを導入した。膜厚20nmの非単結晶GaN層12を堆積した後、トリメチルガリウムの導入を停止した。これを緩衝層として用いた。

【0057】次いで、基板温度を1000℃に昇温し、V族原料としてヒドラジンに加えてアンモニアを導入し、1分後に3族原料としてトリメチルガリウムを導入した。膜厚3μmのGaN層13を成長した後、トリメチルガリウムの導入を停止した。3μm成長すると、GaN層13表面は平坦となり、基板界面から発生した欠陥の伝搬は著しく低減された。次いで、基板温度を800℃に降温し、トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムを同時に導入し、膜厚0.5μmのAl_{0.45}Ga_{0.55}In_{0.05}N層14を成長した。トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムの導入を停止した後、基板温度を降温し300℃以下の温度になったところでヒドラジンとアンモニアの導入を停止した。基板の温度を室温まで降下させた後、石英製反応管1内より基板を取り出した。

【0058】本実施例の場合は、得られた結晶表面は鏡面でホール効果によるとキャリア濃度は 10^{15} cm^{-3} 以下であり、成長温度が800℃と低温でありながら1000℃で成長したGaN層、さらには実施例1の場合よりもより高品質な四元混晶が得られた。また、シリコン基板11表面を炭化することにより、基板界面からの欠陥の発生は著しく抑制された。また、表面を窒化することで容易かつ緻密にGaNが核成長するので、実施例6の場合に比べてさらに欠陥が低減された。

【0059】この形成方法は、サファイア基板を用いた

場合には全く効果は認められず、シリコン基板の場合に極めて有効であった。

【0060】（実施例7）図9に本発明の第七の実施例のAlGaInN薄膜の形成方法により作製したAlGaInN薄膜の断面構造図を示す。図1のMOVPE装置を用いたAlGaInN薄膜の形成方法について、順を追って説明する。

【0061】（111）面GaP基板27を有機洗浄した後、石英製トレー6上に結晶成長基板として配置し、石英製反応管1内に導入した。石英製反応管1内に水素ガスを導入した後、石英製反応管1内圧力を1/10気圧に設定し、グラファイト製サセプター4を800回転/分で回転させた。ホスフィン雰囲気中でグラファイト製サセプター4を800℃まで昇温し、GaP基板27表面の清浄化を行った。ホスフィンの導入を停止し、ヒドラジンを導入し基板表面に窒化層28を形成した。基板温度を600℃まで降温した後、石英製ガス導入管2からGaP基板27面上に3族原料としてトリメチルガリウムを導入した。膜厚20nmの非単結晶GaN層12を堆積した後、トリメチルガリウムの導入を停止した。これを緩衝層として用いた。次いで、基板温度を1000℃に昇温し、V族原料としてヒドラジンに加えてアンモニアを導入し、1分後に3族原料としてトリメチルガリウムを導入した。

【0062】膜厚3μmのGaN層13を成長した後、トリメチルガリウムの導入を停止した。3μm成長すると、GaN層13表面は平坦となり、基板界面から発生した欠陥の伝搬は著しく低減された。次いで、基板温度を800℃に降温し、トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムを同時に導入し、膜厚0.5μmのAl_{0.45}Ga_{0.55}In_{0.05}N層14を成長した。トリメチルガリウム、トリメチルアルミニウムとトリメチルインジウムの導入を停止した後、基板温度を降温し300℃以下の温度になったところでヒドラジンとアンモニアの導入を停止した。基板の温度を室温まで降下させた後、石英製反応管1内より基板を取り出した。

【0063】本発明によれば、得られた結晶表面は鏡面でホール効果によるとキャリア濃度は 10^{15} cm^{-3} 以下であり、基板にGaPを用いたが、サファイア上に形成したAlGaInNと同程度の高品質な四元混晶が得られた。また、GaP基板27表面を窒化することにより、基板界面からの欠陥の発生は著しく抑制され、サファイア基板と同程度まで欠陥が低減された。

【0064】この形成方法は、GaP基板の場合に極めて有効であった。なお、本発明は上述した実施例に限定されるものではない。たとえば、用いる基板は上述の基板には限定されない。また、結晶成長に用いた原料も上述の限りではない。AlGaInN多層膜の構成も限定されるものでない。

【0065】

【発明の効果】このように本発明によれば、窒素原料としてアルキルアミン系、ヒドラジン系もしくはアルキルアミン系、ヒドラジン系とアンモニアの混合原料を用い、基板を高速で回転させるので、窒素空孔などの点欠陥の少ないInを含むAlGaInN薄膜を低温で容易に形成できる。

【0066】また、InNとAlGaInNを交互に形成した超薄膜多層膜によってAlGaInN薄膜を構成するので、より高品質なAlGaInN薄膜を形成できる。

【0067】また、AlGaInN薄膜形成に先立ちAlGaInN歪超格子構造を形成するので、転位の伝搬を著しく低減し高品質なAlGaInN薄膜を形成できる。

【0068】また、組成が連続的に変化する炭化層や窒化層をGaN等の非単結晶層に先立ち形成するので、転位の伝搬を著しく低減しサファイア以外の基板にも高品質なAlGaInNが形成できる。

【0069】したがって、発光効率の高い青色発光ダイオードや情報処理装置用光源などに用いることのできる青色半導体レーザ素子製造に極めて有用である。

【図面の簡単な説明】

【図1】この発明の実施例の形成方法を説明するMOVPE装置の概略図

【図2】この発明の第一の実施例のAlGaInN薄膜の形成方法によるAlGaInN薄膜の断面構造図

【図3】この発明の第二の実施例のAlGaInN多層膜の形成方法によるAlGaInN多層膜の断面構造図

【図4】この発明の第三の実施例のAlGaInN薄膜の形成方法によるAlGaInN薄膜の断面構造図

【図5】この発明の第四の実施例のAlGaInN多層*

* 膜の形成方法によるAlGaInN薄膜の断面構造図

【図6】この発明の第四の実施例の原料ガスの供給手順図

【図7】この発明の第五の実施例のAlGaInN薄膜の形成方法によるAlGaInN薄膜の断面構造図

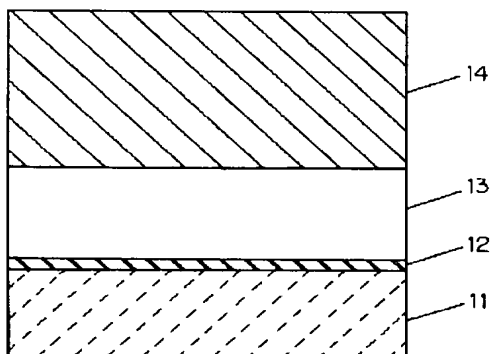
【図8】この発明の第六の実施例のAlGaInN薄膜の形成方法によるAlGaInN薄膜の断面構造図

【図9】この発明の第七の実施例のAlGaInN薄膜の形成方法によるAlGaInN薄膜の断面構造図

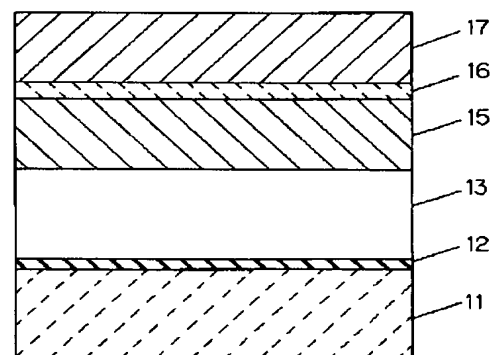
【符号の説明】

- 1 石英製反応管
- 2 石英製ガス導入管
- 3 高周波加熱用コイル
- 4 グラファイト製サセプター
- 5 サセプター支持棒
- 6 石英製トレー
- 7 基板
- 8 排気口
- 11 シリコン基板
- 12 非単結晶GaN層
- 13、21 GaN層
- 14、15、17 $Al_{0.45}Ga_{0.5}In_{0.05}N$ 層
- 16、19 $Ga_{0.9}In_{0.1}N$ 層
- 18 $Al_{0.3}Ga_{0.7}N$ 層
- 20 $Al_{0.3}Ga_{0.7}N/Ga_{0.9}In_{0.1}N$ 歪超格子
- 22 InN層
- 23 AlGaIn層
- 24 擬似的AlGaIn層
- 25 炭化層
- 26、28 窒化層
- 27 GaP基板

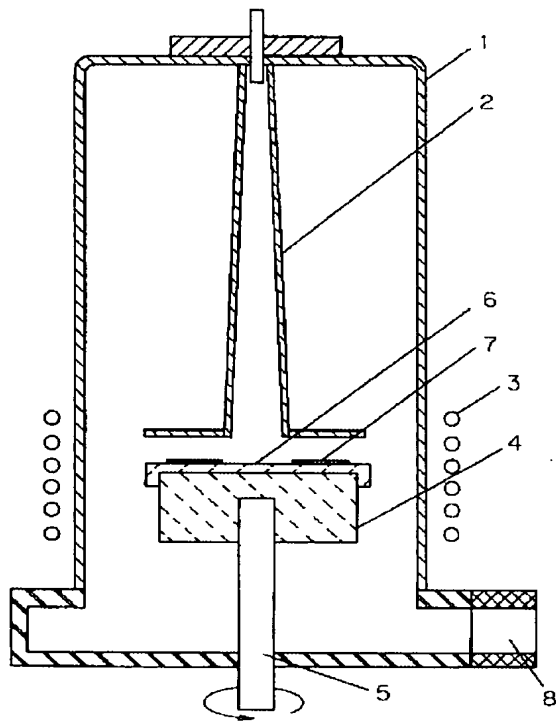
【図2】



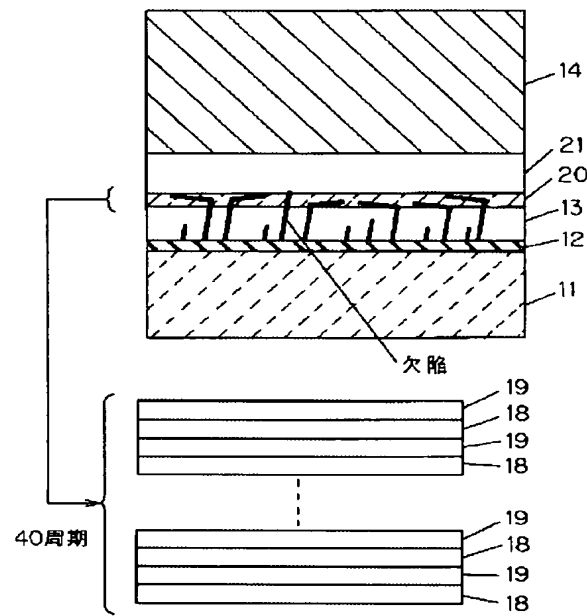
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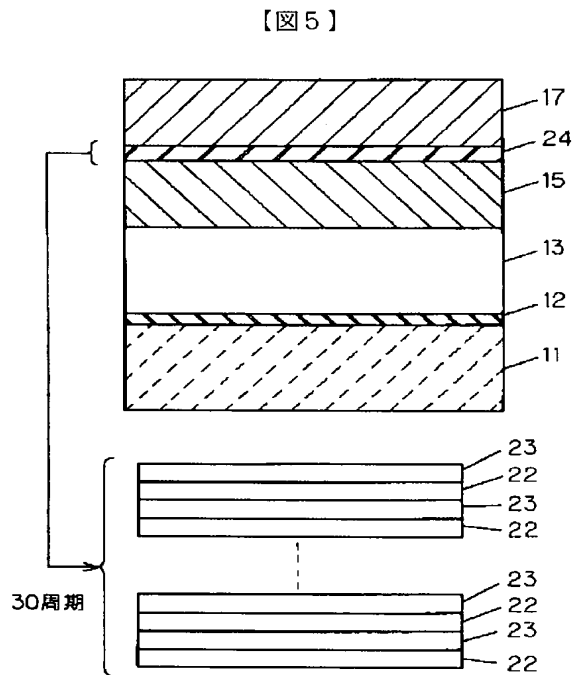
【図1】



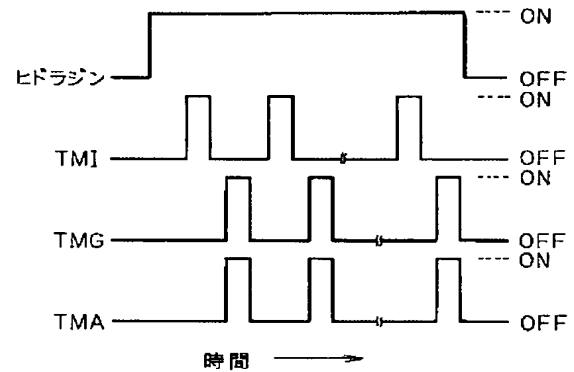
【図4】



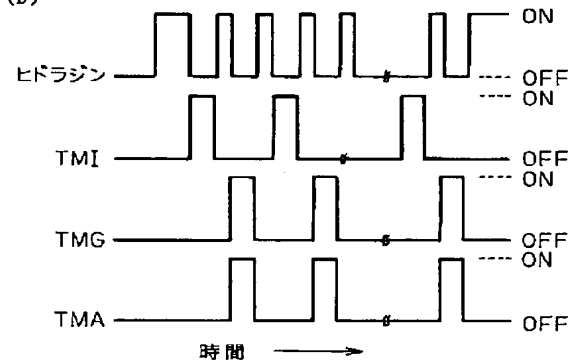
【図6】



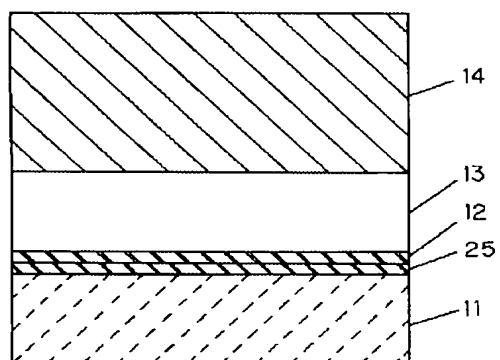
(a)



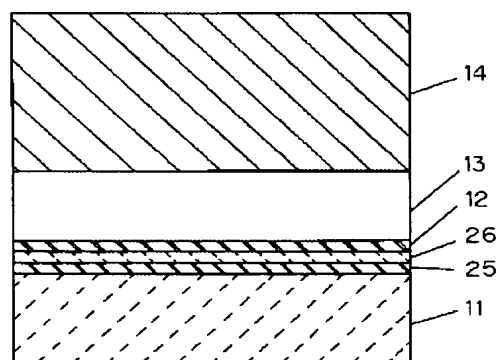
(b)



【図7】



【図8】



【図9】

